



PATENT APPLICATION #1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Docket No: Q62193

Kenichiro SATO, et al.

Appln. No.: 09/729,953

Group Art Unit: 1752

Confirmation No.: 7258

Examiner: J. CHU

Filed: December 6, 2000

For: POSITIVE TYPE PHOTORESIST COMPOSITION

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**SUBMISSION OF SWORN ENGLISH LANGUAGE  
TRANSLATIONS OF PRIORITY DOCUMENTS**

Commissioner for Patents  
Washington, D.C. 20231

Sir:

Submitted herewith are sworn English language translations of Applicants' four Japanese priority documents, JP9-032431, JP9-043974, JP9-048056 and JP9-053583, filed February 17, February 27, March 3, and March 7, 1997, respectively, on which claims to priority are made under 35 U.S.C. §119.

The Examiner is respectfully requested to acknowledge receipt of said priority documents.

Respectfully submitted,

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Date: August 8, 2002

Enclosures (4)

09/023,80  
Q49327  
SATO, et al  
filed 02/13/9

## DECLARATION

I, Kazuhiko OGAWA, residing at 5-12-5, Inodai, Toride-shi, Ibaraki, Japan, hereby declare that I have a thorough knowledge of the English and Japanese languages and that the writing contained in the following pages is an accurate translation of the Japanese Priority Application Hei. 9-43974, filed on February 27, 1997.

Declared at Tokyo, Japan

This 21<sup>st</sup> day of September, 2000



Kazuhiko OGAWA



wherein  $R_1$  to  $R_4$  and  $m$  have the same meanings as given in claim 6;  $R_5$  represents a hydrogen atom or a methyl group; and  $A$  represents one group selected from the group consisting of a single bond, an alkylene group, a substituted alkylene group, an ether group, a thioether group, a carbonyl group, an ester group, an amido group, a sulfonamido group, a urethane group and a urea group, or a combination of two or more of them.

[Claim 3] The positive type photoresist composition described in claim 1 or 2, wherein said resin further contains repeating structure units each having an alicyclic hydrocarbon moiety.

[Claim 4] The positive type photoresist composition described in any one of claims 1 to 3, wherein said resin further contains repeating structure units each having a group which is decomposed by action of an acid to increase solubility in an alkali developing solution.

[Detailed explanation of the invention]

[Technical field to which the invention pertains]

The present invention relates to a positive type photoresist composition suitable for exposure treatment with active light rays or radiation, particularly light rays having a wavelength as very short as 170 nm to 220 nm, and more particularly to a positive type photoresist composition high in sensitivity, and giving an excellent resist pattern and a pattern excellent

in adhesion to a substrate.

[Prior art]

In recent years, there have been glowing demands in the field of production of various electronic devices requiring fine processing such as semiconductor elements towards the devices progressively increased in density and integration. This makes very severe the required performances for the photography techniques for realizing refined patterns. Contributing to this refining technique are photoresists increased in resolution and exposure light having a shortened wavelength.

In general, the resolution (Res) of the optical system can be represented by the Rayleigh equation, namely  $Res = k \cdot \lambda / NA$  (wherein  $k$  is a process factor,  $\lambda$  is a wavelength of an exposure light source, and  $NA$  is the number of openings of a lens). This equation shows that the width of a reproduced line can be decreased to resolve a fine pattern (namely high resolution can be obtained) by shortening the wavelength at the time of exposure. Surely, the exposure wavelength has been sifted to the g-line (436 nm) and the i-line (365 nm) of a high pressure mercury lamp with a decrease in the minimum width of the reproduced line, and the production of the devices by use of the KrF excimer laser beam (249 nm) has been studied. For further fine processing, the use of an excimer laser beam having a shorter wavelength, particularly ArF (193 nm), has a good prospect.

Looking at photoresists exposed to shortwave light, high

integration in multilayer resist systems utilizing surface lithography, not in monolayer resist systems which have previously been used in the industrial production, is also studied. However, it still suffers from the problem of complicated processes which have prevented the practical application of the multilayer resists.

In the case of excimer lasers including KrF excimer lasers, it is generally considered that the life of gases is short, and that the cost performance of the lasers is required to be improved because exposure devices themselves are expensive.

Responding to this are so-called chemical amplification type resists becoming the main current in KrF excimer laser exposure applications. In the chemical amplification type resists, acids are generated from photo acid generators existing in catalytic amounts in the systems by exposure, and protective groups of alkali-soluble groups of binders or low molecular weight compounds are eliminated with the catalytic amount of acids by the catalytic reaction to ensure discrimination of the solubility in alkali developing solutions. In the chemical amplification type resists, the acids generated by the photocatalytic reaction are catalytically utilized, so that an increase in sensitivity is expected.

In general, the chemical amplification system resists can be roughly divided into three classes, commonly called as a 2-component system, a 2.5-component system and a 3-component system. In the 2-component system, a photo acid generator is

combined with a binder resin. The binder resin is a resin having a group which is decomposed by the action of an acid to enhance the solubility of the resin in an alkali developing solution (which is also referred to as an acid decomposable group) in its molecule. The 2.5-component system contains a low molecular weight compound further having an acid decomposable group in addition to such a 2-component system. The 3-component system contains the photo acid generator, the alkali-soluble resin and the above-mentioned low molecular weight compound.

However, when the wavelength of exposure light becomes short, a new problem is encountered. That is, in the photoresists, raw materials good in transparency to shortwave light is poor in resistance to dry etching. On the other hand, there is the problem that raw materials good in resistance to dry etching is poor in transparency. The compatibility of the resistance to dry etching and the transparency is basically the problem of the performance of the binder resins contained in photoresist layers.

The binder resins include novolak resins and poly(p-hydroxystyrene). The novolak resins are widely utilized as alkali-soluble resins for i-line resists, and the poly(p-hydroxystyrene) resins are used as base polymers for KrF excimer laser resists. These produce no problem as long as long-wave light is used. However, different therefrom, the use of shortwave light rises a problem. In particular, the

above-mentioned resins have high optical density within the wavelength region of 170 nm to 220 nm. It is therefore actually difficult to directly use these resins as with the conventional methods. Accordingly, the development of resins high in light transparency and resistance to dry etching has been looked forward to.

One of the general solutions to this problem is a method of introducing, for example, an alicyclic hydrocarbon moiety into the resin. There is also a method of utilizing a naphthalene skeleton, one of the aromatic compounds. In particular, various reports disclose that the introduction of alicyclic hydrocarbon moieties fulfills demands for both light transparency and resistance to dry etching. For example, it is described in Journal of Photopolymer Science and Technology, 3, 439 (1992).

On the other hand, what to select as the acid decomposable group contained in the resin is important, particularly, because it affects the sensitivity and resolution of the resist and further the aging stability.

The acid decomposable groups for protecting carboxylic acid groups, which have hitherto been mainly reported, include tertiary alkyl esters such as t-butyl esters and acetal esters such as tetrahydropyranyl esters and ethoxyethyl esters. However, the t-butyl ester groups have the drawback that the ability of being eliminated with the generated acids is low, resulting in a lowering of the sensitivity. Conversely, the tetrahydropyranyl



esters and the ethoxyethyl esters have a large problem with the aging stability because of their easy decomposition at ordinary temperatures.

Further, JP-A-5-346668 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") has proposed to use 3-oxocyclohexyl ester groups as the acid decomposable groups. However, they are not necessarily satisfactory in sensitivity.

As described above, for the acid decomposable groups for protecting the carboxylic acids which satisfy the sensitivity and the aging stability of the photoresists at the same time, how to design the acid decomposable groups has been not necessarily clear.

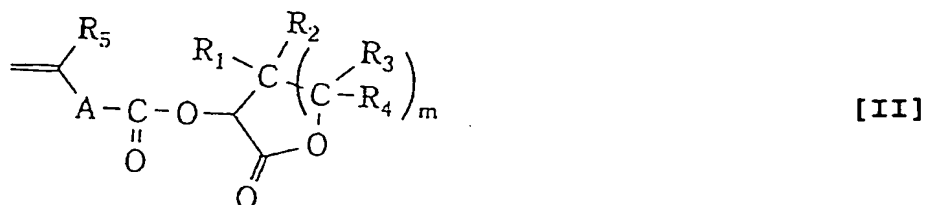
Furthermore, in order to decrease the width of the reproduced line to resolve the fine pattern in the resulting resist pattern, not only the above-mentioned characteristics but also sufficient adhesion of the fine pattern obtained to a substrate is required. Even if the fine pattern is obtained, insufficient adhesion thereof sometimes causes separation thereof.

[Problem to be solved by the invention]

It is therefore an object of the present invention to provide a positive type photoresist composition sufficiently suitable for light, particularly, within the wavelength region of 170 nm to 220 nm, highly sensitive to light, excellent in



repeating structural units corresponding to a monomer represented by the following general formula [II] and is decomposed by action of an acid to increase solubility in an alkali solution:



wherein R<sub>1</sub> to R<sub>4</sub> and m have the same meanings as given in the above (1); R<sub>5</sub> represents a hydrogen atom or a methyl group; and A represents one group selected from the group consisting of a single bond, an alkylene group, a substituted alkylene group, an ether group, a thioether group, a carbonyl group, an ester group, an amido group, a sulfonamido group, a urethane group and a urea group, or a combination of two or more of them.

(3) The positive type photoresist composition described in the above (1) or (2), wherein said resin further contains repeating structural units each having an alicyclic hydrocarbon moiety.

(4) The positive type photoresist composition described in any one of the above (1) to (3), wherein said resin further contains repeating structural units each having a group which is decomposed by action of an acid to increase solubility in an alkali developing solution.

[Mode for carrying out the invention]

The present invention will be described in detail below.

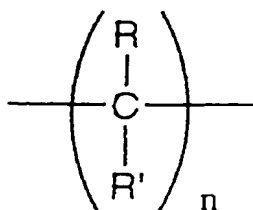
The alkyl groups represented by  $R_1$  to  $R_4$  in general formula [I] are preferably lower alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl and sec-butyl, more preferably, methyl, ethyl, propyl, isopropyl and butyl, and most preferably methyl and ethyl.

$m$  represents 1 or 2, and preferably 1.

Raw material resins for the resins containing the groups represented by the above-mentioned general formula [I] may be any, as long as they provide the effects of the present invention.

In the present invention, as the resins containing the groups represented by general formula [I], the resins containing the repeating structural units represented by the above-mentioned general formula [II] are preferred. These resins can be obtained, for example, by radical polymerization of monomers corresponding to the repeating structural units represented by the above-mentioned general formula [II].

A in the above-mentioned general formula [II] is a single bond, or one group selected from an alkylene group, a substituted alkylene group, an ether group, a thioether group, a carbonyl group, an ester group, an amido group, a sulfonamido group, a urethane group and a urea group, or a combination of two or more of them. The alkylene groups and the substituted alkylene groups represented by A include groups shown below:



wherein R and R', which may be the same or different, each represents a hydrogen atom, an alkyl group, a substituted alkyl group, a halogen atom, a hydroxyl group or an alkoxyl group. The alkyl groups are preferably lower alkyl groups such as methyl, ethyl, propyl, isopropyl and butyl, and more preferably, methyl, ethyl, propyl and isopropyl. Substituent groups of the substituted alkyl groups include halogen atoms and hydroxyl and alkoxyl groups.

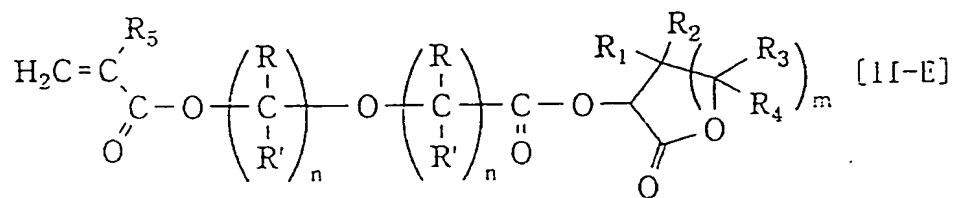
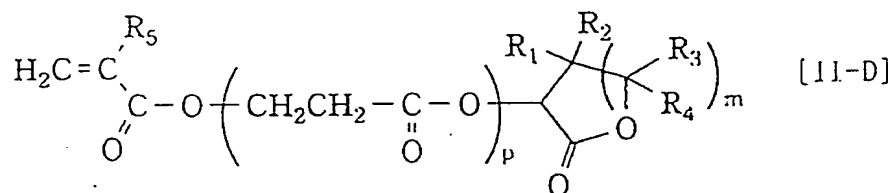
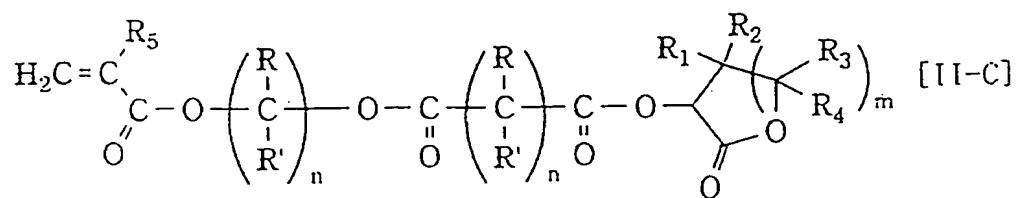
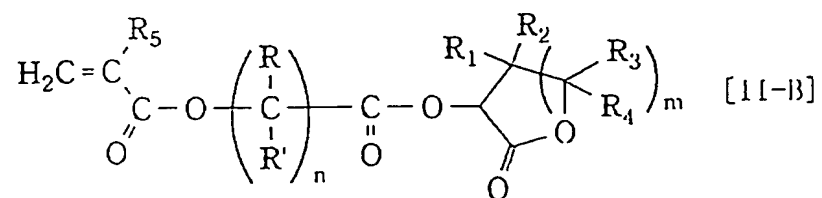
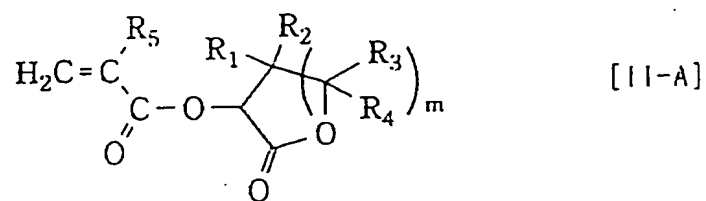
The alkoxyl groups include groups having 1 to 4 carbon atoms such as methoxy, ethoxy, propoxy and butoxy. n represents an integer of 1 to 10.

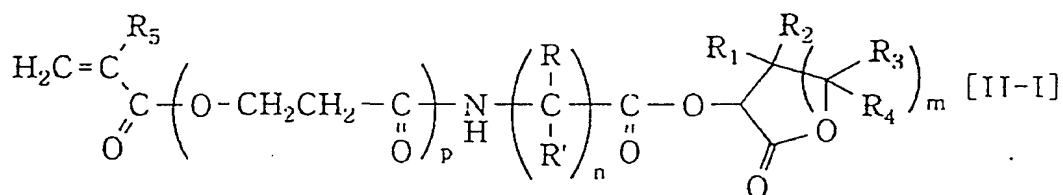
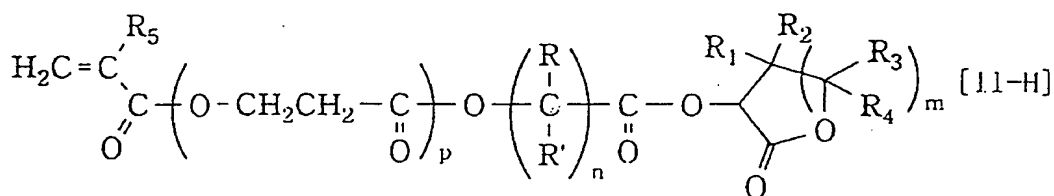
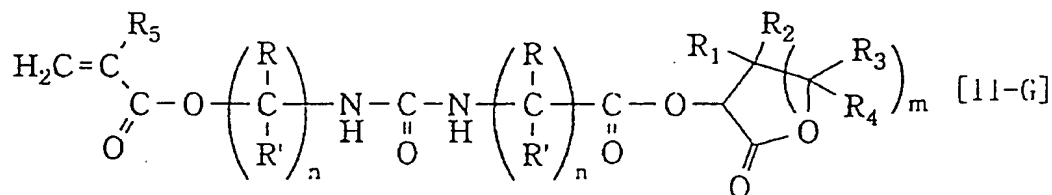
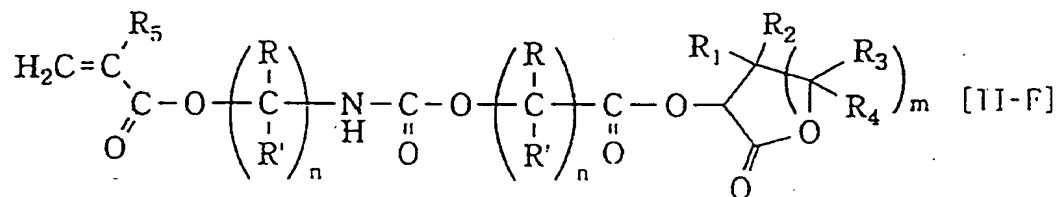
Of the above, A is particularly preferably a single bond, or one group selected from an alkylene group, a substituted alkylene group, an ether group, an ester group, an amido group, a urethane group and a urea group, or a combination of two or more of them.

The alkylene groups and the substituted alkylene groups are preferably alkylene groups each having 1 to 4 carbon atoms herein, and specific examples thereof include methylene, ethylene, propylene, butylene, methyl-substituted methylene, dimethyl-substituted methylene, methyl-substituted ethylene, dimethyl-substituted ethylene, methyl-substituted propylene and

dimethyl-substituted propylene.

Preferred examples of the monomers represented by general formula [II] include monomers represented by the following general formulas [II-A] to [II-I]:

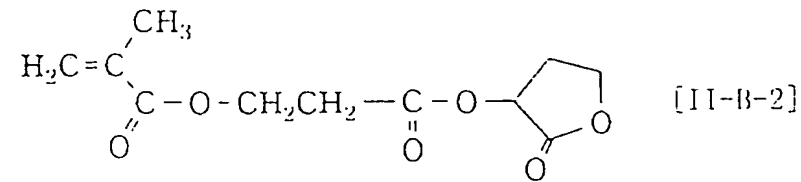
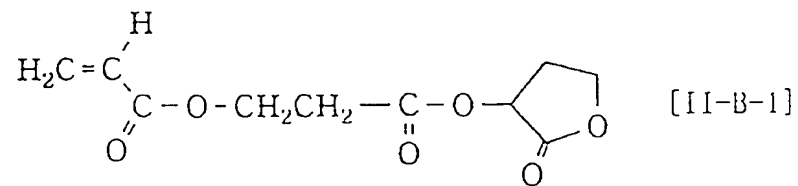
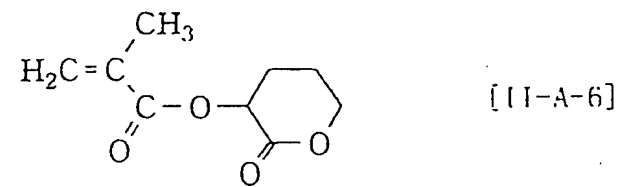
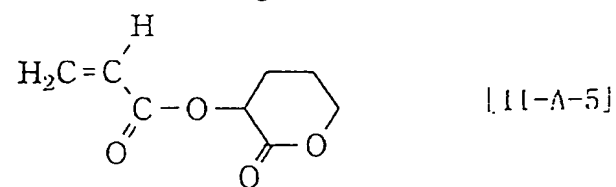
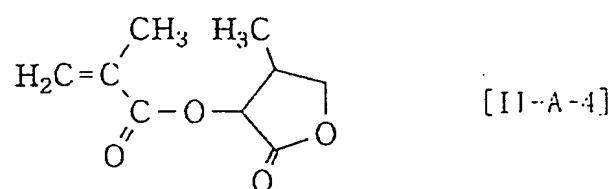
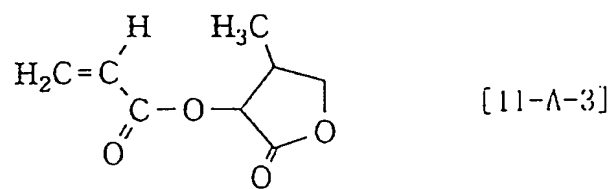
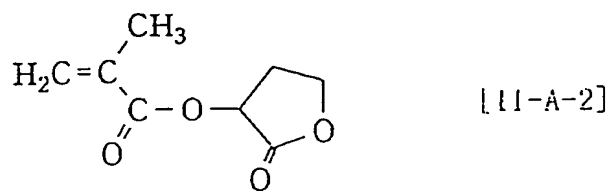
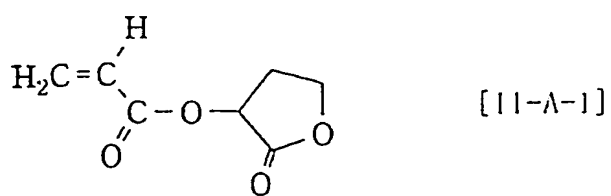


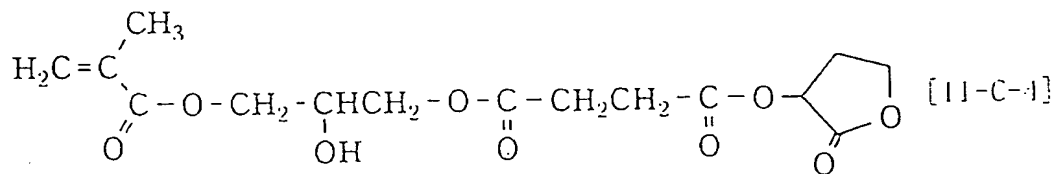
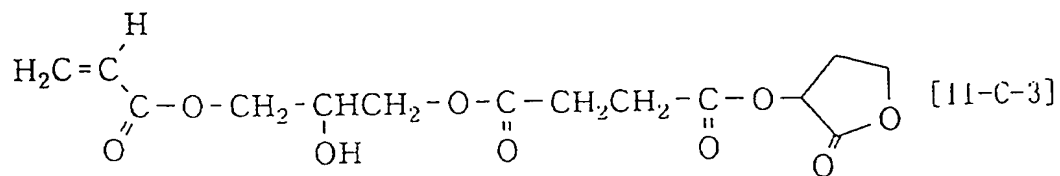
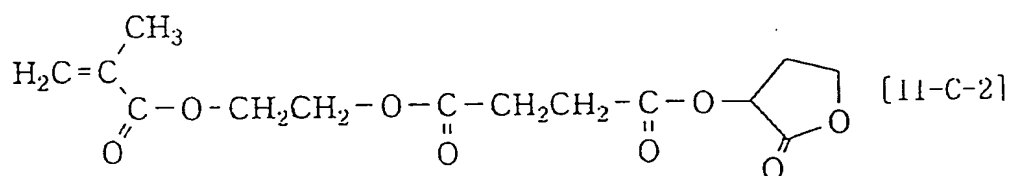
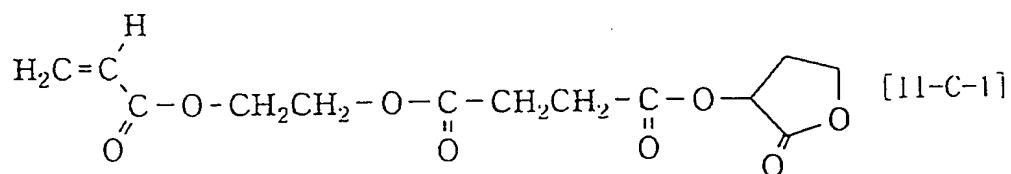
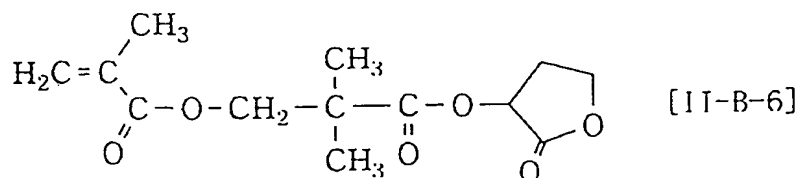
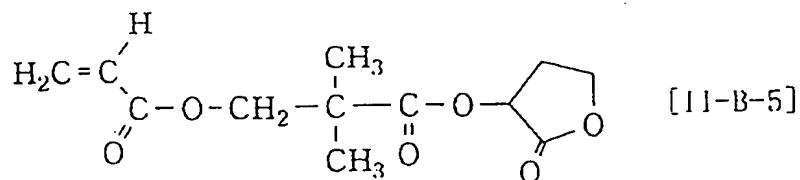
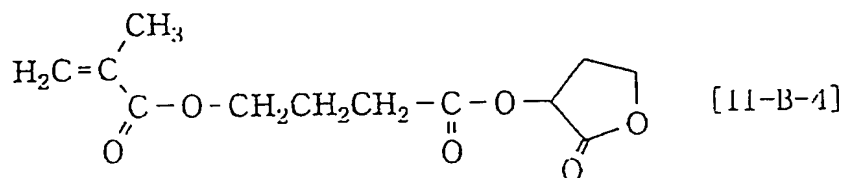
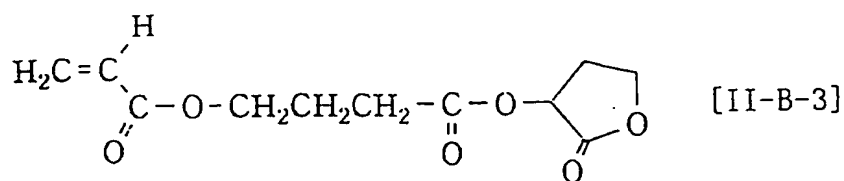


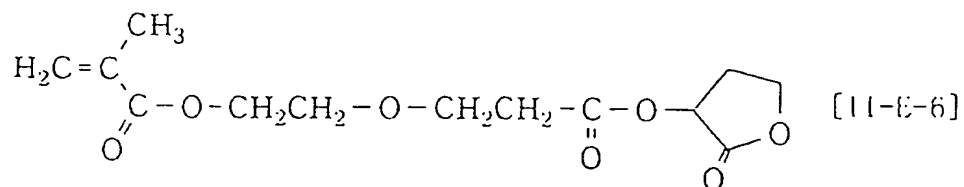
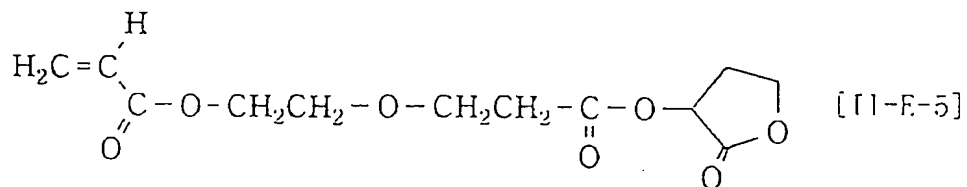
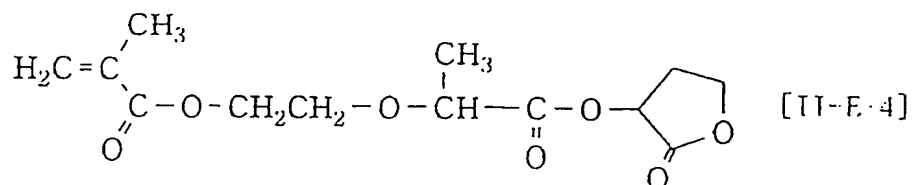
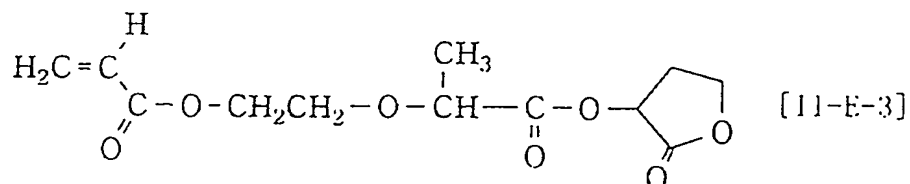
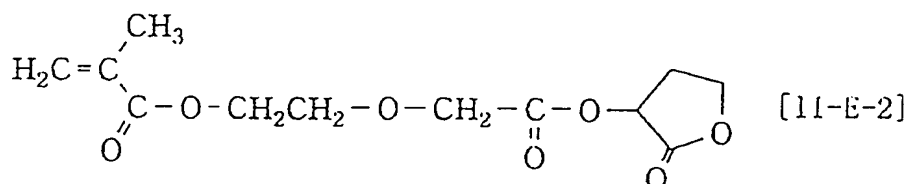
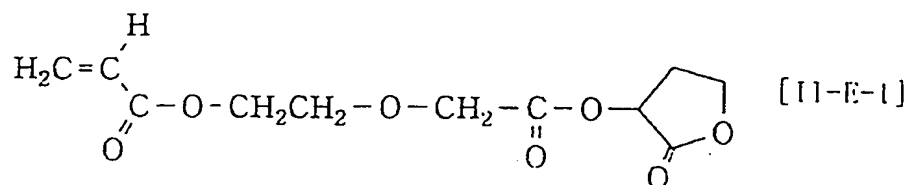
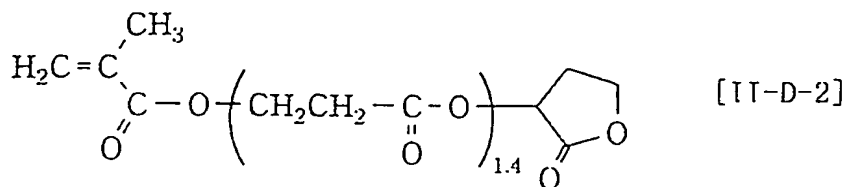
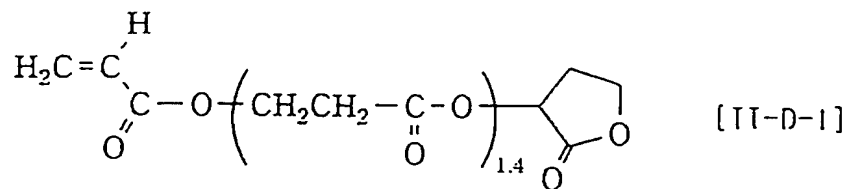
In the above-mentioned general formulas,  $\text{R}_1$  to  $\text{R}_5$ ,  $\text{R}$ ,  $\text{R}'$ ,  $n$  and  $m$  have the same meanings as given above, and  $p$  represents an integer of 1 to 3.

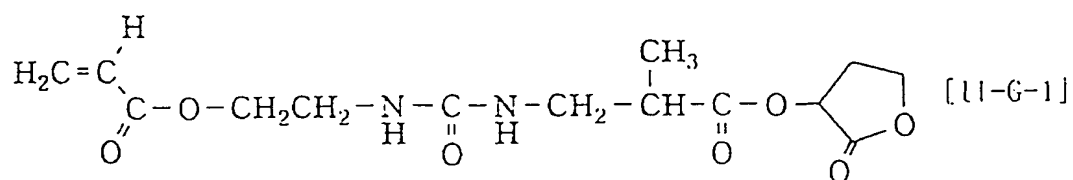
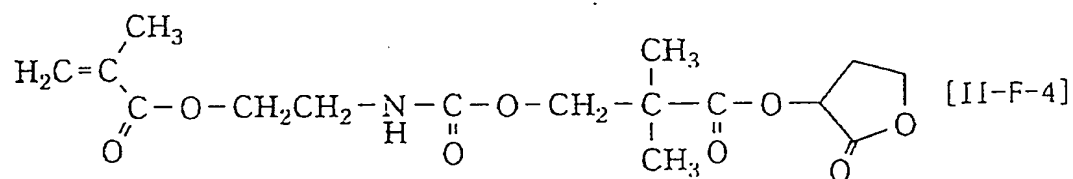
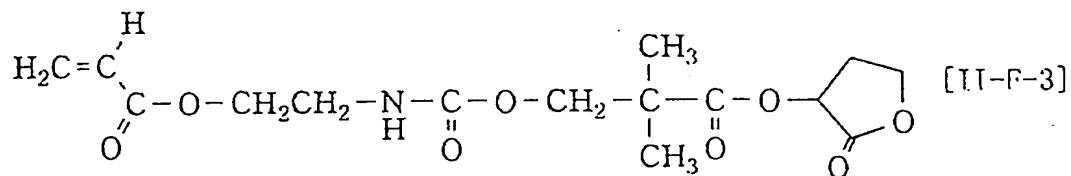
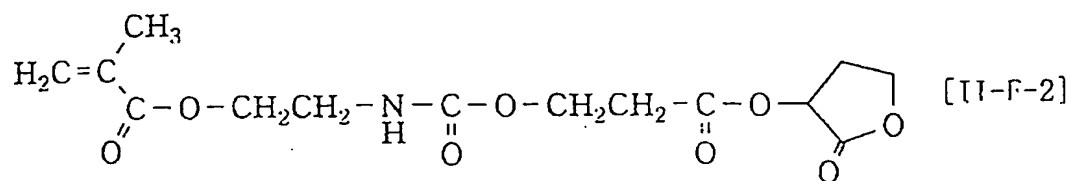
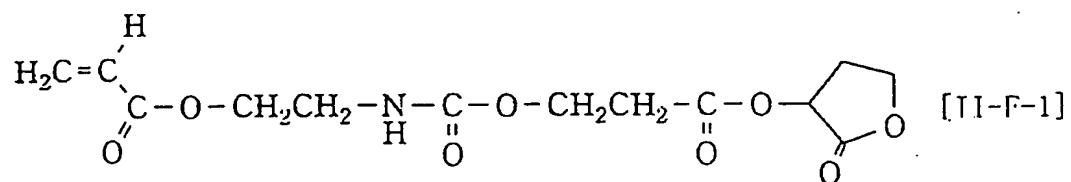
Specific examples of the monomers represented by general formula [II] are enumerated below, but do not limit the scope of the present invention:

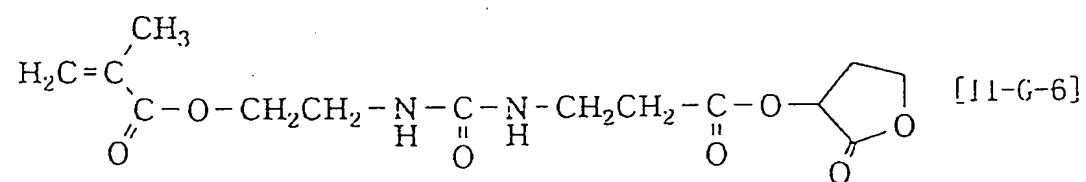
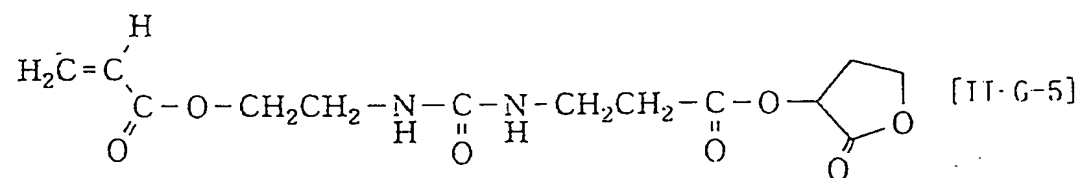
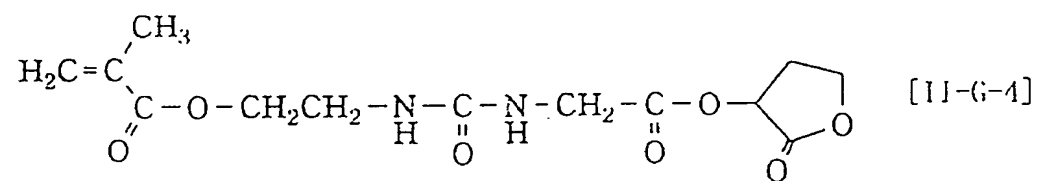
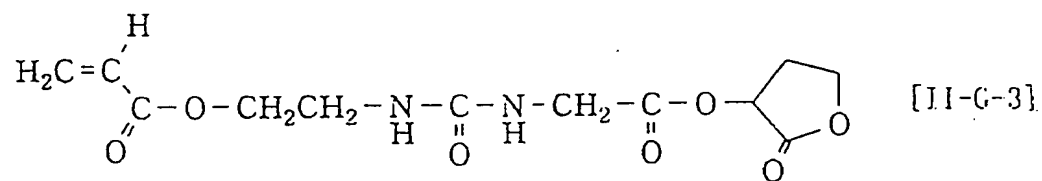
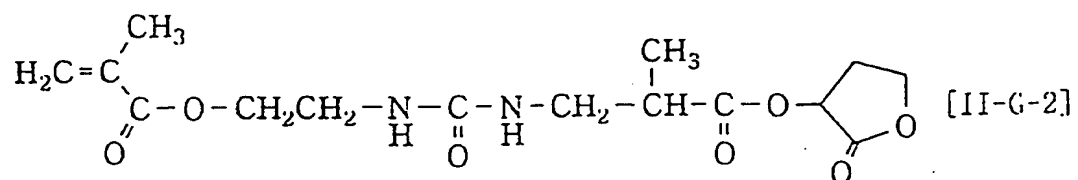


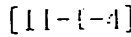
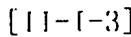
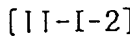
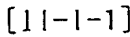
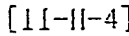
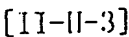
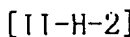
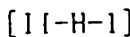






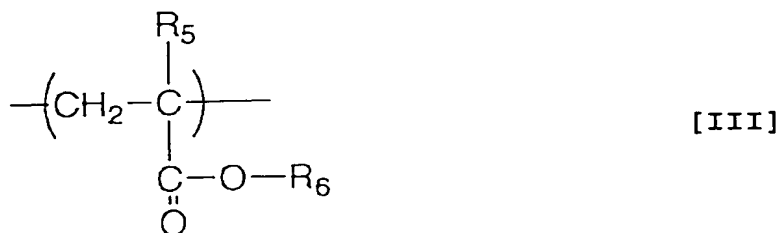


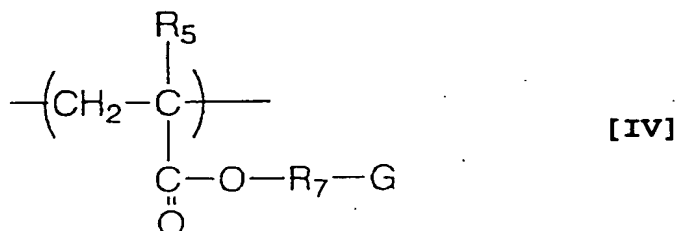




Such monomers represented by general formula [II] can be synthesized by esterifying carboxylic acids having radical-polymerizable carbon-carbon bonds in their molecules with 2-hydroxylactones by the method described in Angew. Chem. int. Ed. Engl., 17, 522 (1978), or by reacting the corresponding carboxylic acid chlorides with 2-hydroxylactones under basic conditions.

It is preferred that the resins used in the positive type photoresist compositions of the present invention contain the repeating units having alicyclic hydrocarbon moieties in their molecules, as well as the groups represented by the above-mentioned general formula [I]. This can enhance the resistance to dry etching of the positive photoresists. The repeating structural units having alicyclic hydrocarbon moieties in their molecules include, for example, repeating structural units represented by the following general formulas [III] and [IV].





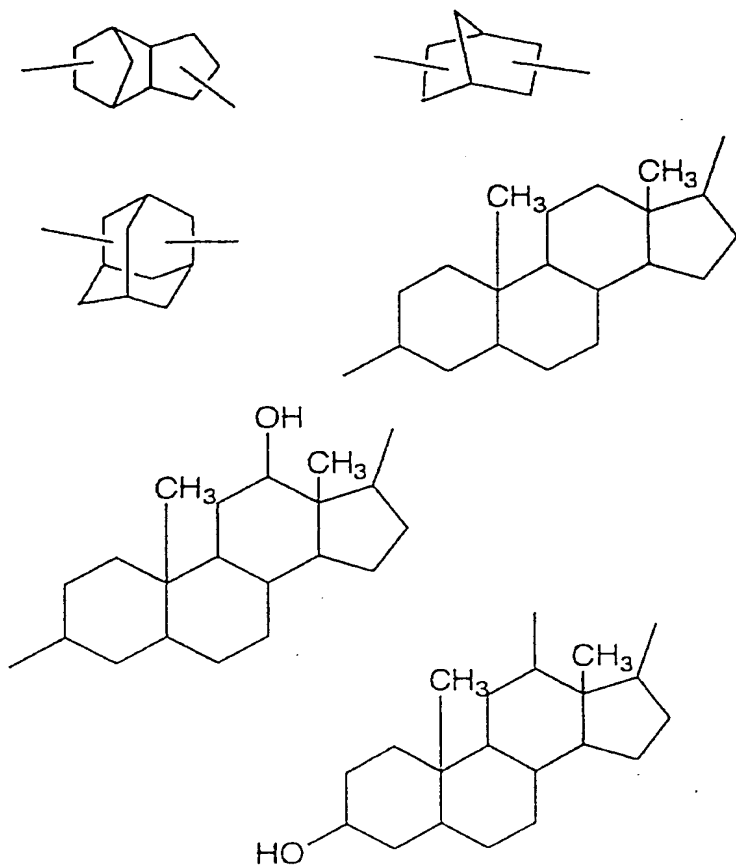
$\text{R}_6$  in general formula [III] is a monovalent alicyclic hydrocarbon group. Specifically, such groups include an adamantyl group, a 2-methyl-2-adamantyl group, a norbornyl group, a bornyl group, an isobornyl group, a tricyclo-decanyl group, a dicyclopentenyl group, a norbornaneepoxy group, a menthyl group, an isomenthyl group and a neomenthyl group.

In general formula [IV],  $\text{R}_7$  is a connecting group having a divalent alicyclic hydrocarbon moiety.  $\text{G}$  represents  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{COOR}_8$  or  $-\text{OR}_8$  wherein  $\text{R}_8$  represents a tertiary alkyl group, a tetrahydropyranyl group, a tetrahydrofuranyl group,  $-\text{CH}_2\text{OR}_9$  or  $-\text{CH}(\text{CH}_3)\text{OR}_9$  wherein  $\text{R}_9$  represents an alkyl group.

$\text{R}_5$  has the same meaning as above.

The alicyclic hydrocarbon moieties contained in the connecting groups represented by  $\text{R}_7$  include, for example, the following structures:





The connecting group in  $R_7$  connecting the above-mentioned alicyclic hydrocarbon moiety and the ester group, or above-mentioned alicyclic hydrocarbon moiety and the group represented by  $G$ , which may be a single bond, includes one group selected from an alkylene group, an ether group, a thioether group, a carbonyl group, an ester group, an amido group and a sulfonamide group, or a combination of two or more of them.

$R_8$  in the  $-\text{COOR}_8$  or  $-\text{OR}_8$  group represents a substituent group decomposable by the action of an acid. Examples of such

groups include tertiary alkyl groups such as t-butyl and t-amyl, 1-alkoxyethyl groups such as tetrahydropyranyl, tetrahydrofuranlyl,  $-\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$  and  $-\text{CH}(\text{CH}_3)\text{OCH}_2\text{CH}(\text{CH}_3)_2$ , and alkoxymethyl groups such as  $-\text{CH}_2\text{OCH}_3$  and  $-\text{CH}_2\text{OCH}_2\text{CH}_3$ .

In the above-mentioned resins, the content of the repeating structural units containing the groups represented by general formula [I] is preferably 3 mol% to 60 mol%, and more preferably 5 mol% to 50 mol%, based on the total repeating units. Less than 3 mol% is unfavorable because the effect of the present invention is difficult to be achieved. Exceeding 60 mol% unfavorably results in liability to deteriorate the resistance to dry etching.

The content of the repeating structural units having alicyclic hydrocarbon moieties in their molecules contained in the resins is 40 mol% to 97 mol%, and preferably 50 mol% to 95 mol%, based on the total repeating units.

It is preferred that the above-mentioned resins used in the present invention further contain groups which are decomposed by the action of acids to increase solubility in alkali developing solutions (also referred to as acid decomposable groups), in addition to the repeating structural units having alicyclic hydrocarbon moieties. This makes the effect of improving sensitivity more significant.

Preferred examples of such acid decomposable groups include  $-\text{COOR}_8$ ,  $-\text{OR}_8$ , a 3-oxocyclohexyl group and a 2-oxocyclohexyl

group as described above.

Specifically, examples thereof include repeating structural units corresponding to conventional monomers such as t-butyl acrylate, t-butylmethacrylate, t-amyl acrylate, t-amyl methacrylate, tetrahydrofuranyl acrylate, tetrahydrofuranyl methacrylate, tetrahydropyranyl acrylate, tetrahydropyranyl methacrylate, alkoxymethyl acrylate, alkoxymethyl methacrylate, 1-alkoxyethyl methacrylate, 3-oxocyclohexyl acrylate, 3-oxocyclohexyl methacrylate, 2-oxocyclohexyl acrylate and 2-oxocyclohexyl methacrylate.

As to the content of the repeating structural units corresponding to the monomers having such conventional acid decomposable groups in the above-mentioned resins, the conventional acid decomposable groups/repeating structural units having groups represented by the above-mentioned general formula [I] is preferably 6/1 or less, and more preferably 3/1 or less.

If this value exceeds 6/1, the effect of the present invention is not sufficiently manifested to bring about an unfavorable result.

Such resins can be further copolymerized with the following monomers as repeating units within the range in which the effect of the present invention can be effectively obtained. However, the present invention is not limited thereto.

This enables fine adjustment of properties required for the above-mentioned resins, particularly (1) solubility in coating

solvents, (2) film forming properties (glass transition temperature), (3) alkali developing properties, (4) film thickness loss (hydrophilic and hydrophobic properties, selection of alkali-soluble groups), (5) adhesion of unexposed areas to substrates and (6) resistance to dry etching.

Such monomers for copolymerization include, for example, compounds each having one addition-polymerizable unsaturated bond, selected from acrylic esters, methacrylic esters, acrylamide compounds, methacrylamide compounds, allyl compounds, vinyl ethers and vinyl esters.

Specifically, examples of the acrylic esters include alkyl acrylates (wherein alkyl groups each preferably has 1 to 10 carbon atoms) (such as methyl acrylate, ethyl acrylate, propyl acrylate, amyl acrylate, cyclohexyl acrylate, ethylhexyl acrylate, octyl acrylate, t-octyl acrylate, chloroethyl acrylate, 2-hydroxyethyl acrylate, 2,2-dimethylhydroxypropyl acrylate, 5-hydroxypentyl acrylate, trimethylolpropane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate, furfuryl acrylate and tetrahydrofurfuryl acrylate).

Examples of the methacrylic esters include alkyl methacrylates (wherein alkyl groups each preferably has 1 to 10 carbon atoms) (such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, chlorobenzyl methacrylate, octyl methacrylate, 2-hydroxyethyl

methacrylate, 4-hydroxybutyl methacrylate, 5-hydroxypentyl methacrylate, 2,2-dimethyl-3-hydroxypropyl methacrylate, trimethylolpropane monomethacrylate, pentaerythritol monomethacrylate, furfuryl methacrylate and tetrahydrofurfuryl methacrylate).

Examples of the acrylamide compounds include acrylamide, N-alkylacrylamides (wherein alkyl groups each preferably has 1 to 10 carbon atoms, for example, methyl, ethyl, propyl, butyl, t-butyl, heptyl, octyl, cyclohexyl and hydroxyethyl), N,N-dialkylacrylamides (wherein alkyl groups each preferably has 1 to 10 carbon atoms, for example, methyl, ethyl, butyl, isobutyl, ethylhexyl and cyclohexyl), N-hydroxyethyl-N-methylacrylamide and N-2-acetamidoethyl-N-acetylacrylamide.

Examples of the methacrylamide compounds include methacrylamide, N-alkylmethacrylamides (wherein alkyl groups each preferably has 1 to 10 carbon atoms, for example, methyl, ethyl, t-butyl, ethylhexyl, hydroxyethyl and cyclohexyl), N,N-dialkylmethacrylamides (wherein alkyl groups are, for example, ethyl, propyl and butyl) and N-hydroxyethyl-N-methylmethacrylamide.

Examples of the allyl compounds include allyl esters (such as allyl acetate, allyl caproate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate and allyl lactate) and allyloxyethanol.

Examples of the vinyl ethers include alkyl vinyl ethers (such as hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether, diethylene glycol vinyl ether, dimethylaminoethyl vinyl ether, diethylaminoethyl vinyl ether, butylaminoethyl vinyl ether, benzyl vinyl ether and tetrahydrofurfuryl vinyl ether).

Examples of the vinyl esters include vinyl butyrate, vinyl isobutyrate, vinyl trimethylacetate, vinyl diethylacetate, vinyl valerate, vinyl caproate, vinyl chloroacetate, vinyl dichloroacetate, vinyl methoxyacetate, vinyl butoxyacetate, vinyl acetoacetate, vinyl lactate, vinyl  $\beta$ -phenylbutyrate and vinyl cyclohexylcarboxylate.

The monomers also include dialkyl itaconates (such as dimethyl itaconate, diethyl itaconate and dibutyl itaconate), dialkyl esters of maleic acid or fumaric acid (such as dimethyl maleate and dibutyl fumarate) and monoalkyl esters thereof, acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic anhydride, maleimide, acrylonitrile, methacrylonitrile and maleylonitrile.

In addition, any monomers may be used, as long as they are addition-polymerizable unsaturated compounds copolymerizable with the repeating structural units represented by general formula

The content of the repeating structural units corresponding to the additional monomers as described above is preferably 99 mol% or less, more preferably 90 mol% or less, and most preferably 80 mol% or less, based on the total molar number of the repeating structural units represented by general formula [I] and the repeating structural units having alicyclic hydrocarbon moieties. Exceeding 99 mol% is unfavorable because the effect of the present invention is not sufficiently manifested.

$$\begin{array}{ccccccccccc} \text{---}(\text{CH}_2\text{---}\overset{\text{R}_5}{\underset{\text{A}}{\underset{\text{C=O}}{\underset{\text{O}}{\text{C}}}}}\text{---})_a(\text{CH}_2\text{---}\overset{\text{R}_5}{\underset{\text{C=O}}{\underset{\text{O}}{\underset{\text{R}_6}}{\text{C}}}}\text{---})_b(\text{CH}_2\text{---}\overset{\text{R}_5}{\underset{\text{C=O}}{\underset{\text{O}}{\underset{\text{R}_7}}{\underset{\text{G}}{\text{C}}}}}\text{---})_c(\text{CH}_2\text{---}\overset{\text{R}_5}{\underset{\text{C=O}}{\underset{\text{O}}{\underset{\text{R}_{10}}{\text{C}}}}\text{---})_d(\text{CH}_2\text{---}\overset{\text{R}_5}{\underset{\text{C=O}}{\underset{\text{O}}{\underset{\text{R}_{11}}{\text{C}}}}\text{---})_e(\text{CH}_2\text{---}\overset{\text{R}_5}{\underset{\text{C=O}}{\underset{\text{O}}{\underset{\text{OH}}{\text{C}}}}}\text{---})_f\text{---} \\ \text{O} \\ \text{O} \\ \text{R}_1 \\ \text{R}_2 \\ \text{R}_4 \text{ R}_3 \text{ m} \end{array}$$

- 29 -

represents a methyl group, an ethyl group, a propyl group, an iso-propyl group or a n-butyl group; a is 5 to 80; b is 0 to 70; c is 0 to 95; d, e and f are each 0 to 50;  $a+d \geq 5$ ;  $b+c \geq 40$ ; and  $a+b+c+d+e+f = 100$ .

The weight-average molecular weight of the above-mentioned resins used in the present invention is preferably 2,000 to 200,000. If the weight-average molecular weight is less than 2,000, deterioration in heat resistance and resistance to dry etching is unfavorably observed. Exceeding 200,000 brings about unfavorable results such as deterioration in developing properties, and deterioration in film forming properties caused by an extreme increase in viscosity.

The resins used in the present invention can be synthesized by usual methods including radical polymerization using azo compounds as initiators.

The positive type photoresist compositions of the present invention mainly contain the above-mentioned resins and photo acid generators. The amount of the resin added to the whole composition is 40% to 99% by weight, and preferably 50% to 97% by weight, based on the total solid content of the resist.

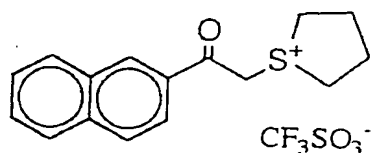
Then, the photo acid generators contained in the positive type photoresist compositions of the present invention are described below.

The photo acid generators are required to satisfy two properties, namely (1) transparency to exposure light (in the

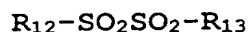


case that the agents have no photobleaching property) and (2) sufficient photodecomposability for ensuring resist sensitivity.

Although guidelines for molecular design for fulfilling such conflicting requirements are not clear in the present circumstances, examples of the photo acid generators include aliphatic alkylsulfonium salts having 2-oxocyclohexyl groups described in JP-A-7-25846, JP-A-7-28237, JP-A-7-92675 and JP-A-8-27102, and N-hydroxysuccinimide sulfonates. Further, examples thereof include sulfonium salts represented by the following general formula (VI), disulfones represented by the following general formula (VII) and compounds represented by the following general formula (VIII), which are described in J. Photopolym. Sci. Technol., 7 (3), 423 (1994).



(VI)



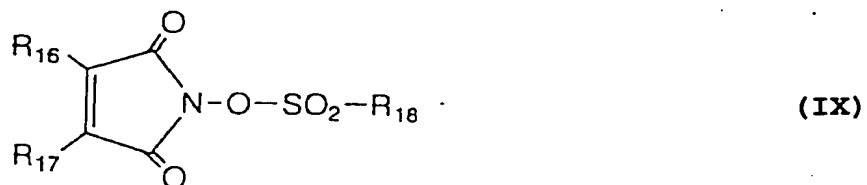
(VII)



(VIII)

wherein  $R_{12}$  to  $R_{15}$ , which may be the same or different, each represents an alkyl group or a cyclic alkyl group.

Further, N-hydroxymaleinimide sulfonates represented by the following general formula (IX) are also preferred.



wherein  $R_{16}$  and  $R_{17}$ , which may be the same or different, each represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, or a cycloalkyl group having 6 or less carbon atoms, and  $R_{16}$  and  $R_{17}$  may combine together by an alkylene group to form a ring; and  $R_{18}$  represents an alkyl group, a perfluoroalkyl group, a cycloalkyl group or a camphor substituent. Such N-hydroxymaleinimide sulfonates are particularly preferred in photosensitivity.

In the above-mentioned general formula (IX), the alkyl groups each having 1 to 6 carbon atoms represented by  $R_{16}$  and  $R_{17}$  include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl and n-hexyl. Particularly, methyl, ethyl and propyl are preferred, and methyl and ethyl are more preferred.

The cycloalkyl groups each having 6 or less carbon atoms include cyclopropyl, cyclopentyl and cyclohexyl. Cyclopentyl and cyclohexyl are preferred. Examples of the formation of rings with  $R_{16}$  and  $R_{17}$  by alkylene chains include the formation of cyclohexyl, norbornyl and tricyclodecanyl groups.

The alkyl groups represented by  $R_{18}$  include straight-chain alkyl groups each having 1 to 20 carbon atoms, including methyl,

ethyl and propyl, and branched alkyl groups each having 1 to 20 carbon atoms, including isopropyl, isobutyl, tert-butyl and neopentyl. Straight-chain or branched alkyl groups each having 1 to 16 carbon atoms are preferred, and straight-chain or branched alkyl groups each having 4 to 15 carbon atoms are more preferred.

The perfluoroalkyl groups include straight-chain perfluoroalkyl groups each having 1 to 20, including trifluoromethyl and pentafluoroethyl, and branched perfluoroalkyl groups each having 1 to 20, including heptafluoroisopropyl and nonafluoro-tert-butyl.

Straight-chain or branched perfluoroalkyl groups each having 1 to 16 carbon atoms are preferred. The cyclic alkyl groups include monocyclic alkyl groups such as cyclopentyl and cyclohexyl, and polycyclic alkyl groups such as decalyl, norbornyl and tricyclodecanyl.

The amount of such a photo acid generators added to the composition is preferably 0.1% to 20% by weight, more preferably 0.3% to 15% by weight, and most preferably 1% to 10% by weight, based on the total solid content of the positive type photoresist composition.

In the positive type photoresist compositions of the present invention, photo acid generators as described below may be used in combination, in addition to the above-mentioned photo acid generators.

The following photo acid generators which can be used in combination are added to the compositions preferably in an

amount of not more than 2% by weight, and more preferably in an amount of not more than 1% by weight, per the solid content of the whole positive type photoresist composition.

Examples of such photo acid generators include diazonium salts described in S. I. Schlesinger, Photogr. Sci. Eng., 18, 387 (1974) and T. S. Bal et al., Polymer, 21, 423 (1980), ammonium salts described in U.S. Patents 4,069,055, 4,069,056 and Re 27,992, and Japanese patent application No. Hei-3-140140, phosphonium salts described in D. C. Necker et al., Macromolecules, 17, 2468 (1984), C. S. Wen et al., Tec. Ptoc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988), U.S. Patents 4,069,055 and 4,069,056, iodonium salts described in J. V. Crivello et al., Macromolecules, 10 (6), 1307 (1977), Chem. & Eng. News, Nov. 28, 31 (1988), European Patents 104,143, U.S. Patents 339,049 and 410,201, JP-A-2-150848 and JP-A-2-296514, sulfonium salts described in J. V. Crivello et al., Polymer, J. 17, 73 (1985), J. V. Crivello et al., J. Org. Chem., 43, 3055 (1978), W. R. Watt et al., J. Polymer Sci., Polymer Chem. Ed., 22, 1789 (1984), J. V. Crivello et al., Polymer Bull., 14, 279 (1985), J. V. Crivello et al., Macromolecules, 14 (5), 1141 (1981), J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 2877 (1979), European Patents 370,693, 3,902,114, 233,567, 297,443 and 297,442, U.S. Patents 3,902,114, 4,933,377, 161,881, 410,201, 339,049, 4,760,013, 4,734,444 and 2,833,827, and German Patents 2,904,626, 3,604,580 and 3,604,581, selenonium salts described in J. V. Crivello et al., Macromolecules,

10 (6), 1307 (1977) and J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 1047 (1979), onium salts such as arsonium salts described in C. S. Wen et al., Tec. Ptoc. Conf. Rad. Curing ASIA, p. 478, Tokyo, Oct. (1988), organic halogen compounds described in U.S. Patent 3,905,815, JP-B-46-4605 (the term "JP-B" as used herein means an "examined Japanese patent publication"), JP-A-48-36281, JP-A-55-32070, JP-A-60-239736, JP-A-61-169835, JP-A-61-169837, JP-A-62-58241, JP-A-62-212401, JP-A-63-70243 and JP-A-63-298339, organic metal/organic halides described in K. Meier et al., J. Rad. Curing, 13 (4), 26 (1986), T. P. Gill et al., Inorg. Chem., 19, 3007 (1980), D. Astruc, Acc. Chem. Res., 19 (12), 377 (1986) and JP-A-2-161445, photo acid generators having o-nitrobenzyl type protective groups described in S. Hayase et al., J. Polymer Sci., 25, 753 (1987), E. Reichmanis et al., J. Polymer Sci., Polymer Chem. Ed., 23, 1 (1985), Q. Q. Zhu et al., J. Photochem., 36, 85, 39, 317 (1987), B. Amit et al., Tetrahedron Lett., (24), 2205 (1973), D. H. R. Barton et al., J. Chem. Soc., 35, 71 (1965), P. M. Collins et al., J. Chem. Soc., Perkin I, 1695 (1975), M. Rudinstein et al., Tetrahedron Lett., (17), 1445 (1975), J. W. Walker et al., J. Am. Chem. Soc., 110, 7170 (1988), S. C. Busman et al., J. Imaging Technol., 11 (4), 191 (1985), H. M. Houlihan et al., Macromolecules, 21, 2001 (1988), P. M. Collins et al., J. Chem. Soc., Chem. Commun., 532 (1972), S. Hayase et al., Macromolecules, 18, 1799 (1985), E. Reichmanis et al., J. Electrochem. Soc., Solid State Sci. Technol.,

130 (6), F. M. Houlihan et al., Macromolecules, 21, 2001 (1988), European Patents 290,750, 046,083, 156,535, 271,851 and 388,343, U.S. Patents 3,901,710 and 4,181,531, JP-A-60-198538 and JP-A-53-133022, compounds producing sulfonic acids by photolysis which are represented by iminosulfonates described in M. Tunooka et al., Polymer Preprints Japan, 35 (8), G. Berner et al., J. Rad. Curing, 13 (4), W. J. Mijs et al., Coating Technol., 55 (697), 45 (1983), Akzo, H. Adachi et al., Polymer Preprints Japan, 37 (3), European Patents 199,672, 84,515, 199,672, 44,115, and 101,122, U.S. Patents 618,564, 4,371,605 and 4,431,774, JP-A-64-18143, JP-A-2-245756 and Japanese patent application No. Hei-3-140109, and disulfone compounds described in JP-A-61-166544.

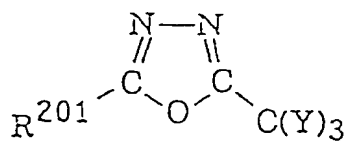
Further, compounds in which these groups or compounds generating acids with light are introduced into their main chains or side chains can be used. Examples of such compounds are described in M. E. Woodhouse et al., J. Am. Chem. Soc., 104, 5586 (1982), S. P. Pappas et al., J. Imaging Sci., 30 (5), 218 (1986), S. Kondo et al., Makromol. Chem., Rapid Commun., 9, 625 (1988), Y. Yamada et al., Makromol. Chem., 152, 153, 163 (1972), J. V. Crivello et al., J. Polymer Sci., Polymer Chem. Ed., 17, 3845 (1979), U.S. Patent 3,849,137, German Patent 3,914,407, JP-A-63-26653, JP-A-55-164824, JP-A-62-69263, JP-A-63-146038, JP-A-63-163452, JP-A-62-153853 and JP-A-63-146029.

Further, compounds generating acids with light can also

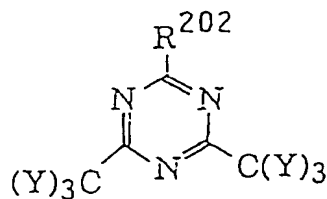
be used which are described in V. N. R. Pillai Synthesis, (1) 1 (1980), A. Abad et al., Tetrahedron Lett., (47), 4555 (1971), D. H. R. Barton et al., J. Chem. Soc., (C), 329 (1970), U.S. Patent 3,779,778 and European Patent 126,712.

Of the above-mentioned compounds which can be used in combination and are decomposed by irradiation of active light rays or radiation to generate acids, compounds particularly effectively used are described below.

(1) Oxazole derivatives substituted by trihalomethyl groups, which are represented by the following general formula (PAG1), or S-triazine derivatives represented by the following general formula (PGA2)



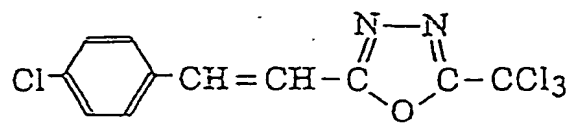
(PAG1)



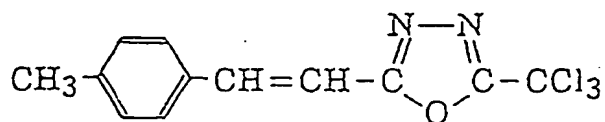
(PGA2)

wherein  $R^{201}$  represents a substituted or unsubstituted aryl or alkenyl group;  $R^{202}$  represents a substituted or unsubstituted aryl, alkenyl or alkyl group, or  $-C(Y)_3$ ; and Y represents a chlorine atom or a bromine atom.

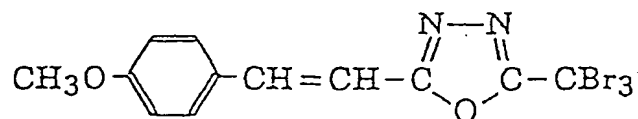
Specific examples thereof include but are not limited to the following compounds:



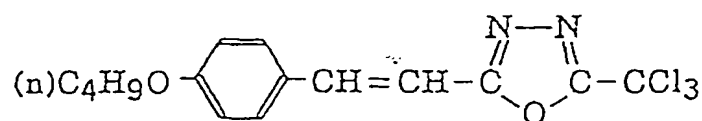
(PAG1-1)



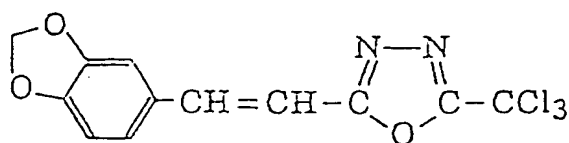
(PAG1-2)



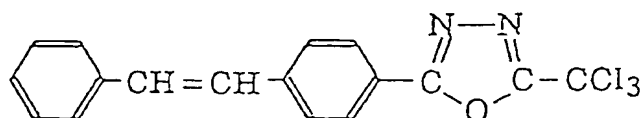
(PAG1-3)



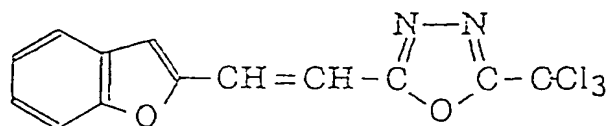
(PAG1-4)



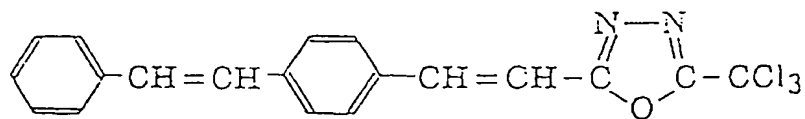
(PAG1-5)



(PAG1-6)

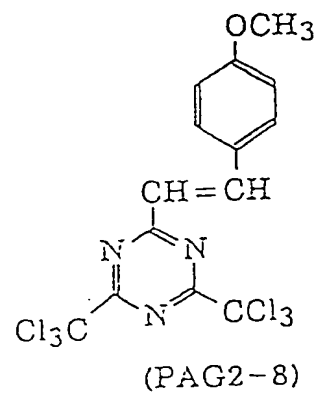
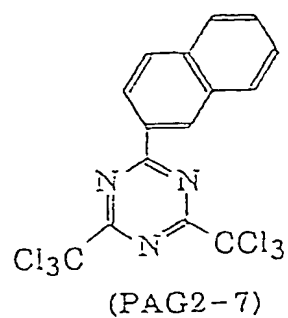
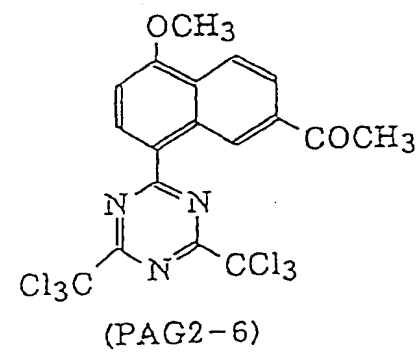
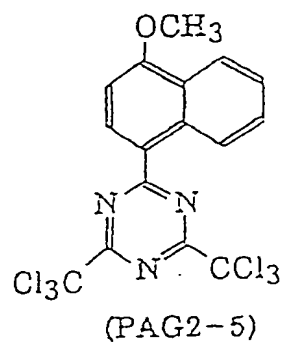
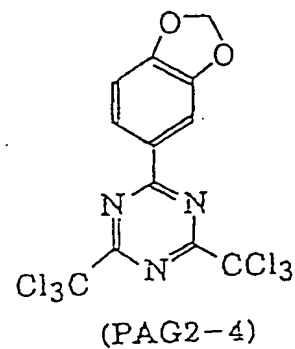
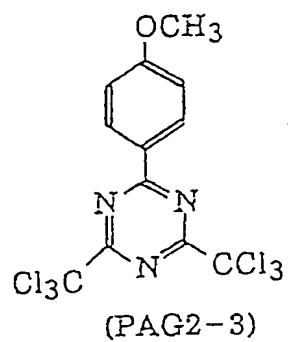
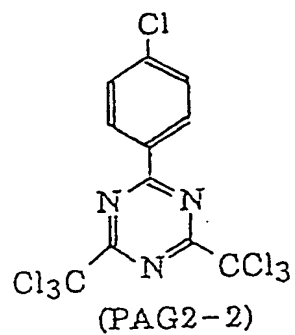
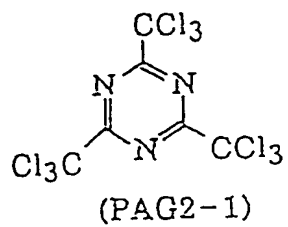


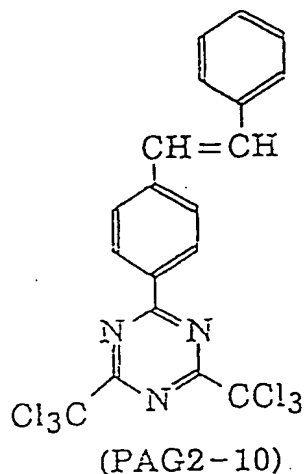
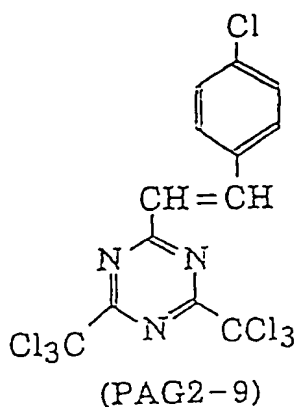
(PAG1-7)



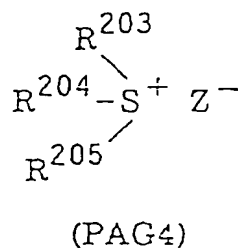
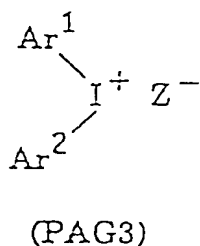
(PAG1-8)







(2) Iodonium salts represented by the following general formula (PAG3) or sulfonium salts represented by the following general formula (PAG4)



wherein  $\text{Ar}^1$  and  $\text{Ar}^2$  each independently represents a substituted or unsubstituted aryl group. Preferred examples of the substituent groups include alkyl, haloalkyl, cycloalkyl, aryl, alkoxyl, nitro, carboxyl, alkoxycarbonyl, hydroxyl, mercapto and halogen atoms.

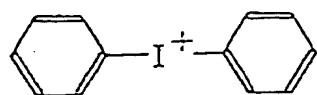
$\text{R}^{203}$ ,  $\text{R}^{204}$  and  $\text{R}^{205}$  each independently represents a substituted or unsubstituted alkyl or aryl group, and preferably

an aryl group having 6 to 14 carbon atoms, an alkyl group having 1 to 8 carbon atoms or a substituted derivative thereof. Preferred examples of the substituent groups for aryl include alkoxyl of 1 to 8 carbon atoms, alkyl of 1 to 8 carbon atoms, nitro, carboxyl, hydroxyl and halogen atoms, and preferred examples thereof for alkyl include alkoxyl of 1 to 8 carbon atoms, carboxyl and alkoxycarbonyl.

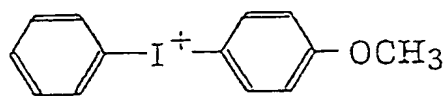
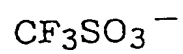
$Z^-$  represents a counter ion such as a perfluoroalkane-sulfonic acid anion, for example,  $CF_3SO_3^-$ , or a pentafluoro-benzenesulfonic acid anion.

Two of  $R^{203}$ ,  $R^{204}$  and  $R^{205}$ , and  $Ar^1$  and  $Ar^2$  may combine together by each single bond or substituent group.

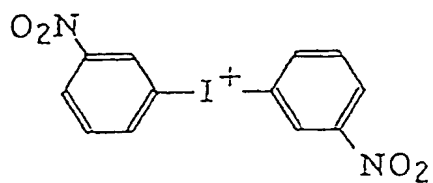
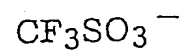
Specific examples thereof include but are not limited to the following compounds:



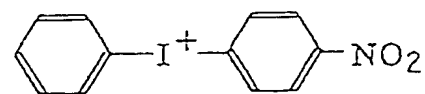
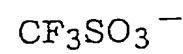
(PAG3-1)



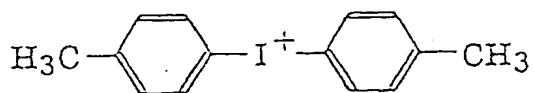
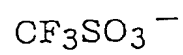
(PAG3-2)



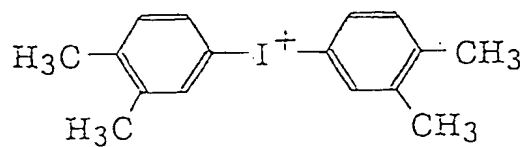
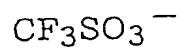
(PAG3-3)



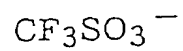
(PAG3-4)

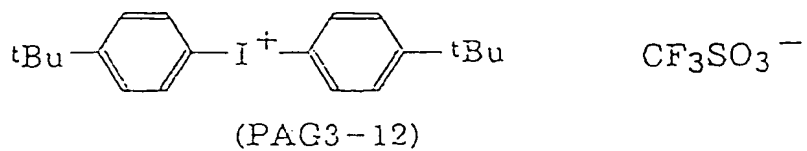
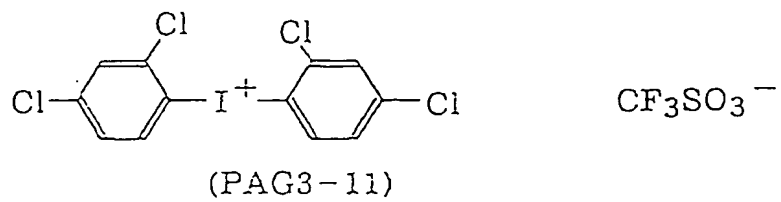
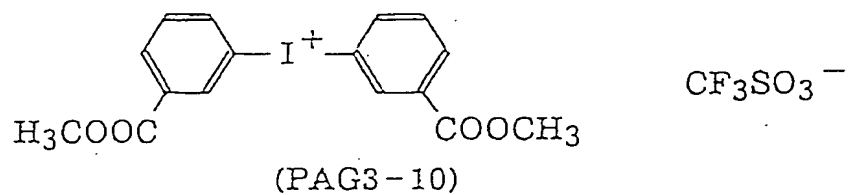
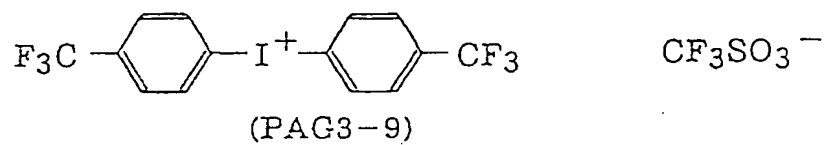
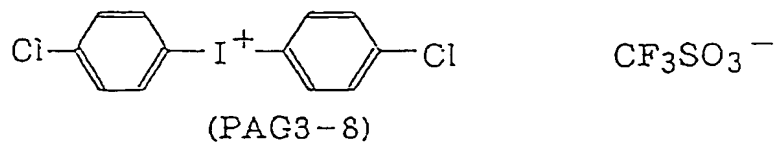
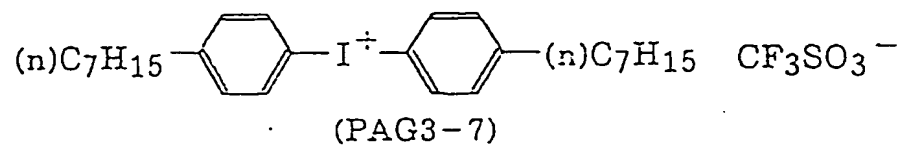


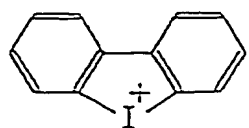
(PAG3-5)



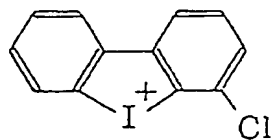
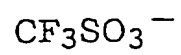
(PAG3-6)



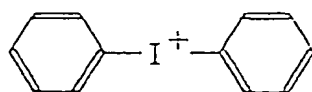
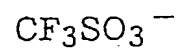




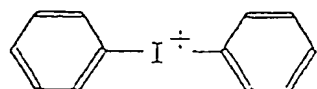
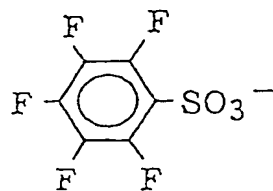
(PAG3-13)



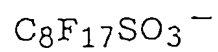
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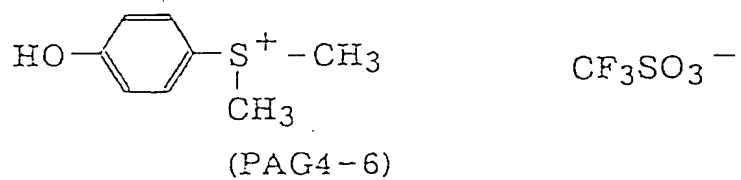
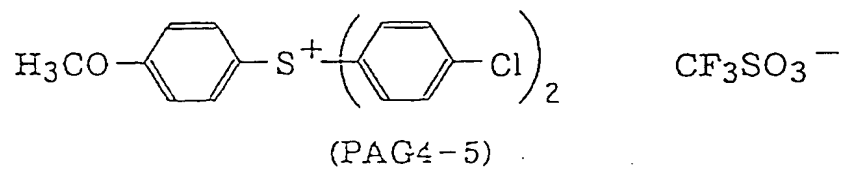
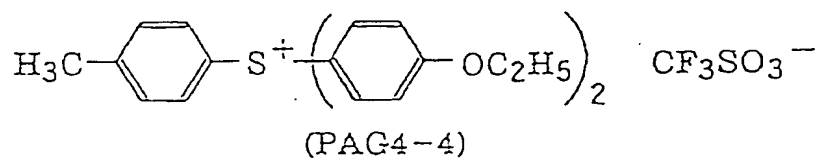
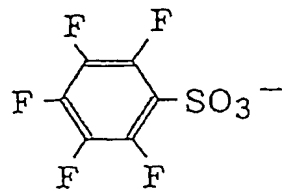
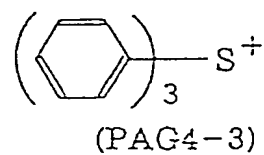
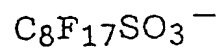
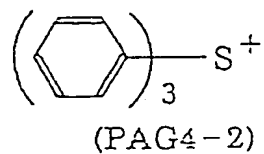
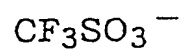
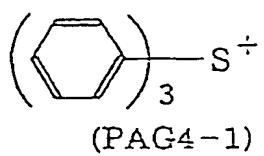


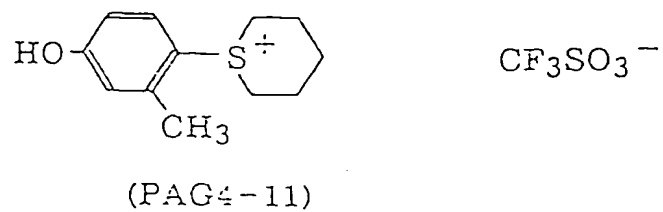
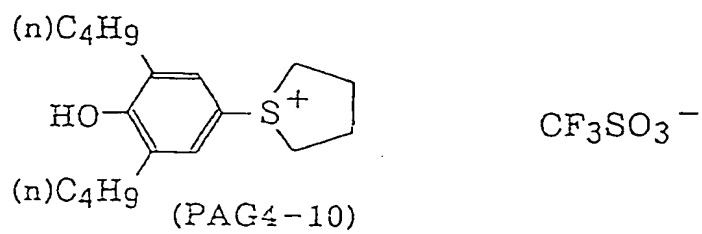
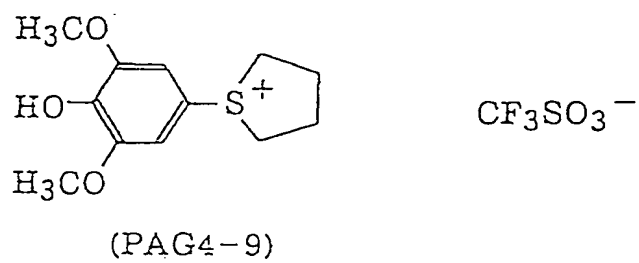
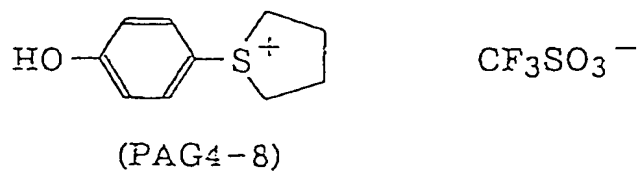
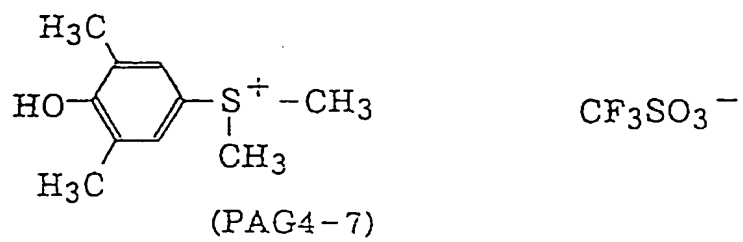
(PAG3-15)



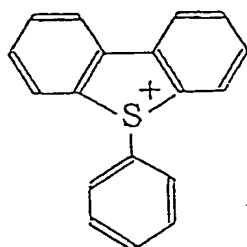
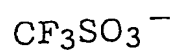
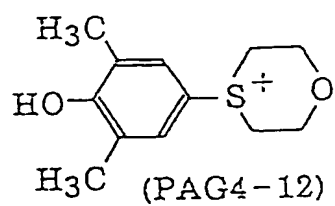
(PAG3-16)



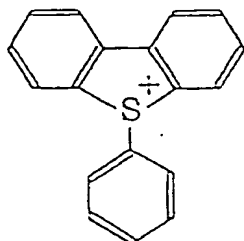
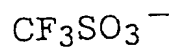




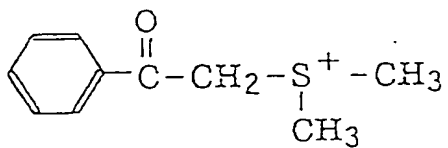
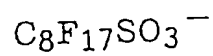




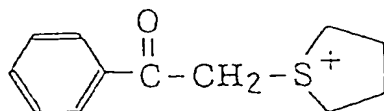
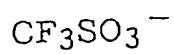
(PAG4-13)



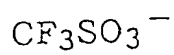
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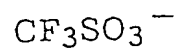
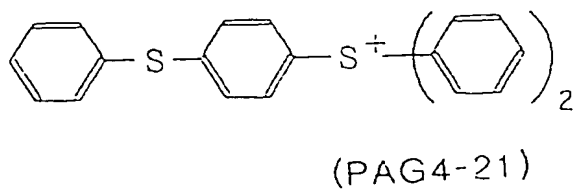
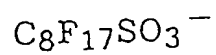
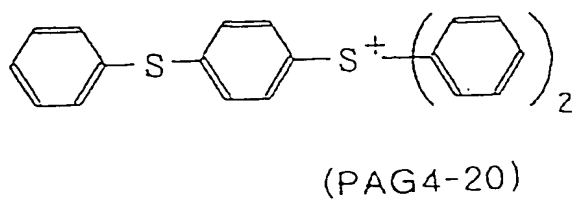
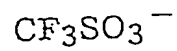
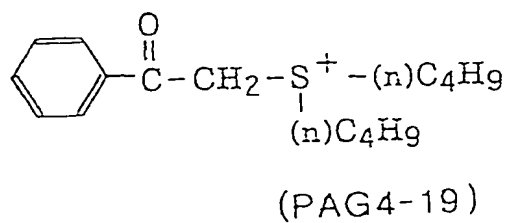
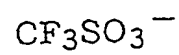
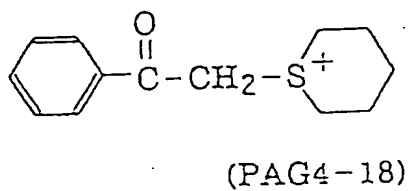
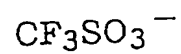
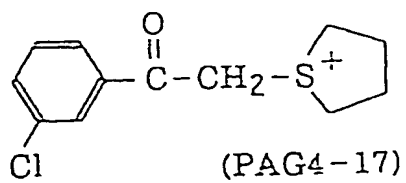


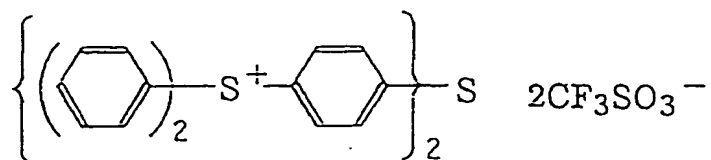
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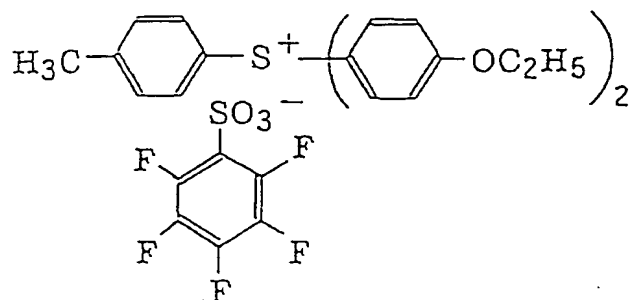
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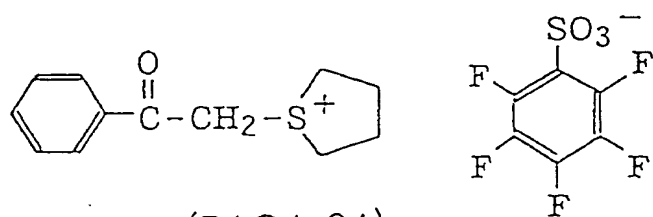




(PAG4-22)



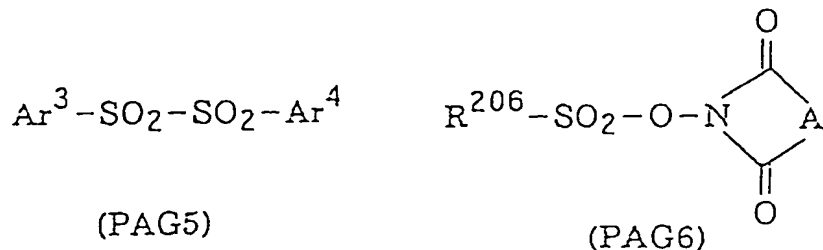
(PAG4-23)



The above-mentioned onium salts represented by general formulas (PAG3) and (PAG4) are known, and can be synthesized, for example, by methods described in J. W. Knapczyk et al., J. Am. Chem. Soc., **91**, 145 (1969), A. L. Maycok et al., J. Org. Chem., **35**, 2532 (1970), E. Goethas et al., Bull. Soc. Chem. Belg., **73**, 546 (1964), H. M. Leicester, J. Am. Chem. Soc., **51**, 3587 (1929), J. V. Crivello et al., J. Polymer Chem. Ed., **18**, 2677

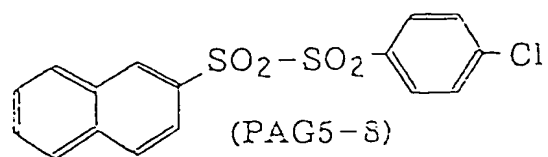
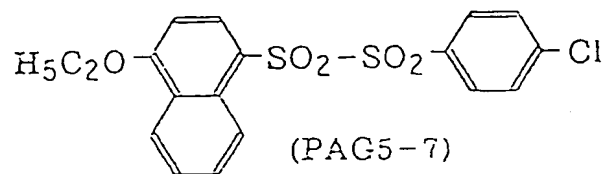
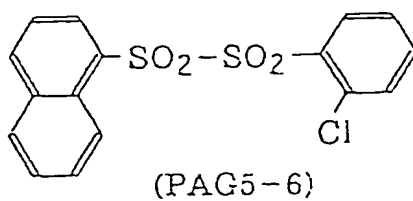
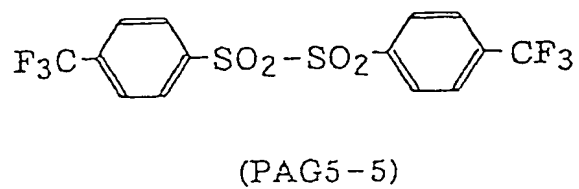
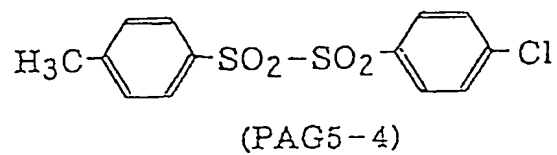
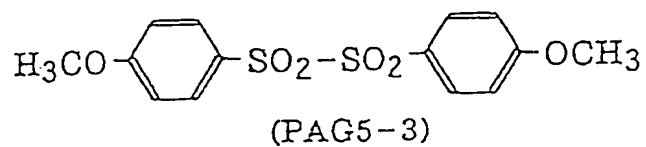
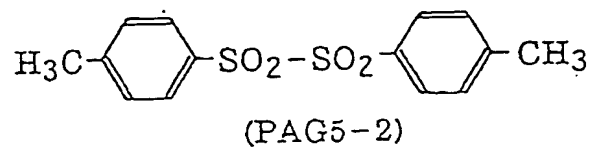
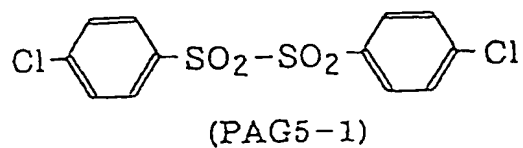
(1980), U.S. Patents 2,807,648 and 4,247,473, and JP-A-53-101331.

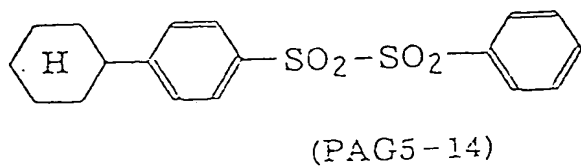
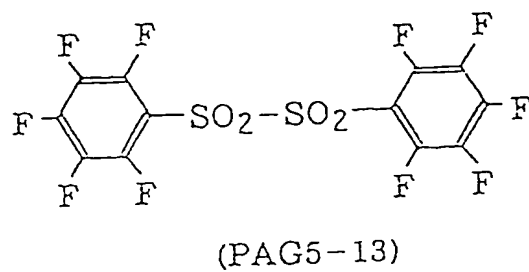
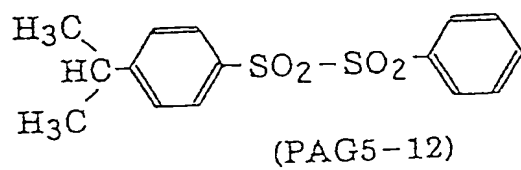
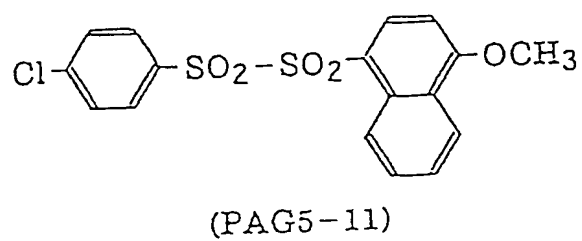
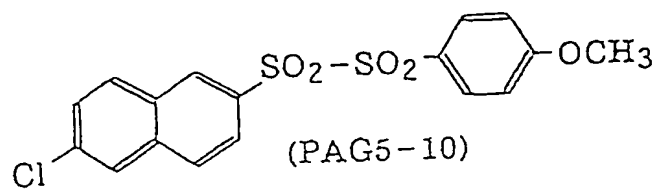
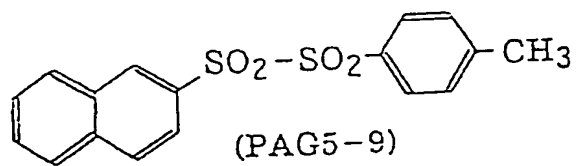
(3) Disulfone derivatives represented by the following general formula (PAG5) or iminosulfonate derivatives represented by the following general formula (PAG6)

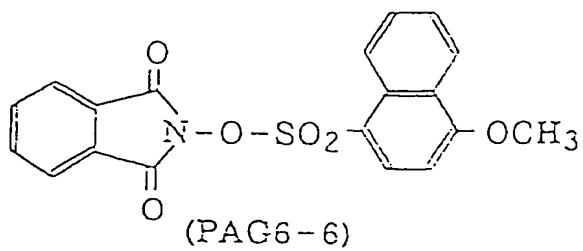
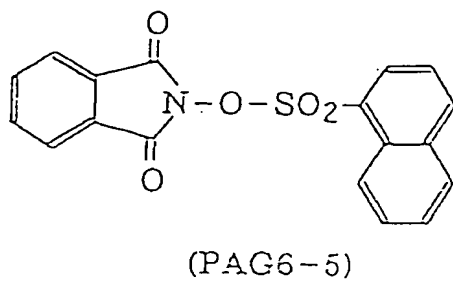
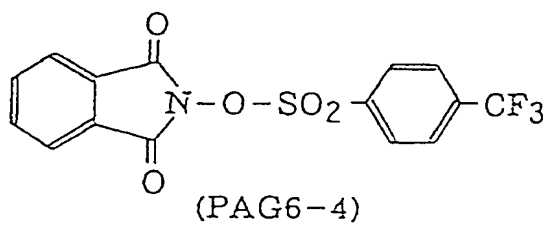
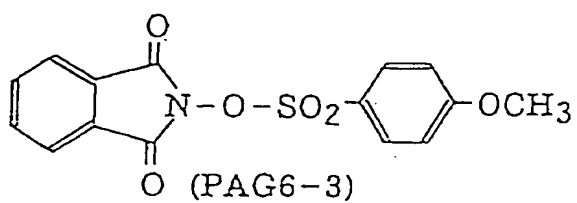
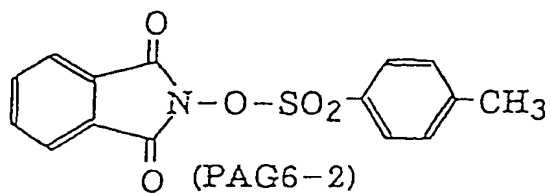
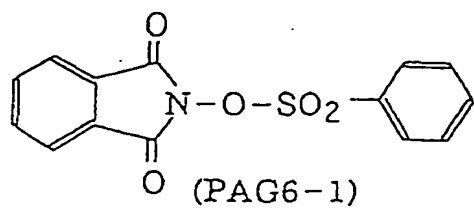


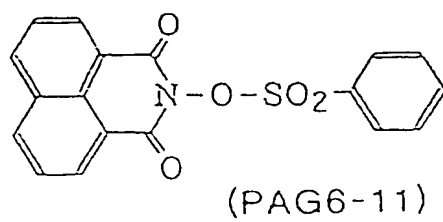
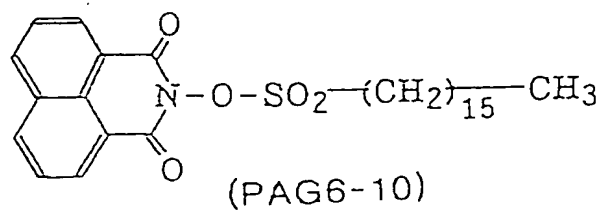
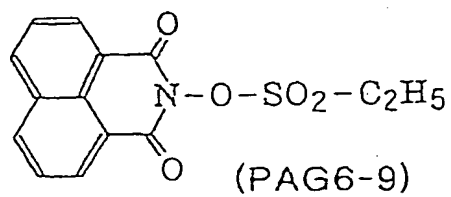
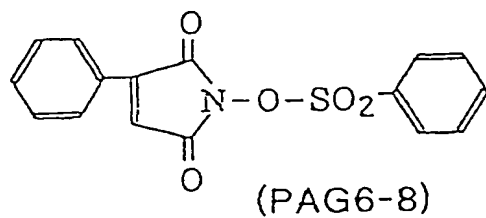
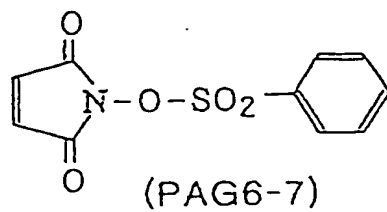
wherein  $\text{Ar}^3$  and  $\text{Ar}^4$  each independently represents a substituted or unsubstituted aryl group;  $\text{R}^{206}$  represents a substituted or unsubstituted alkyl or aryl group; and A represents a substituted or unsubstituted alkylene, alkenylene or arylene group.

Specific examples thereof include but are not limited to the following compounds:

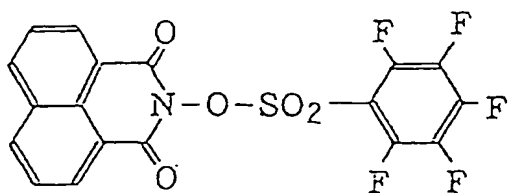
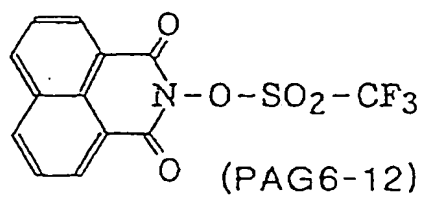




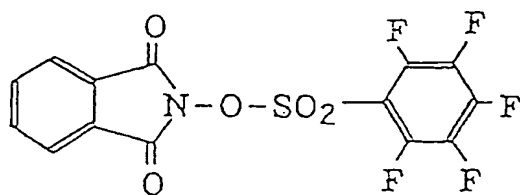








(PAG6-13)



(PAG6-14)

Appropriate alkali-soluble low molecular weight compounds may be added to the positive type photoresist compositions for improving alkali solubility in the systems or controlling the glass transition temperature of the systems to prevent the films from becoming brittle and the heat resistance from being deteriorated. The alkali-soluble low molecular weight compounds include compounds having acidic groups in their molecules such as dialkylsulfonamide compounds, dialkylsulfonylimide ( $-\text{SO}_2-\text{NH}-\text{CO}-$ ) compounds and dialkyldisulfonylimide ( $-\text{SO}_2-\text{NH}-\text{SO}_2-$ ) compounds. The content of the alkali-soluble low molecular weight compound is preferably 40% by weight or less, more preferably 30% by weight or less, and most preferably 25% by weight or less, based on the binder resin.

The compositions of the present invention are preferably used as solutions thereof in specific solvents. Such solvents may be any, as long as they are organic solvents which sufficiently dissolve the respective solid components and can provide the solutions forming uniform coated films by methods such as spin coating. Further, they may be used alone or as a mixture of two or more of them. Specific examples thereof include but are not limited to n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, t-butyl alcohol, methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monoethyl ether acetate, methyl lactate, ethyl lactate, 2-methoxybutyl acetate, 2-ethoxyethyl acetate, methyl pyruvate, ethyl pyruvate, methyl 3-methoxypropionate,

ethyl 3-methoxypropionate, N-methyl-2-pyrrolidinone, cyclohexanone, cyclopentanone, cyclohexanol, methyl ethyl ketone, 1,4-dioxane, ethylene glycol monomethyl ether, ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether, ethylene glycol monoisopropyl ether, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether and 2-heptanone.

The positive type photoresist compositions of the present invention may further contain other components such as surfactants, pigments, stabilizers, coating improvers and dyes, if necessary.

Such positive type photoresist compositions of the present invention are applied onto substrates to form thin films. The thickness of the coated films is preferably 0.4  $\mu\text{m}$  to 1.5  $\mu\text{m}$ .

As exposure means, ones in which the exposure wavelength is included within the range of 170 nm to 220 nm, such as ArF excimer laser stepper exposure, are preferred, and ArF excimer laser stepper exposure is particularly preferred.

#### [Examples]

The present invention will hereinafter be described in more detail by reference to examples. However, the present invention is not limited thereto.

### SYNTHESIS EXAMPLE 1

#### Synthesis of Monomer [II-A-2]

Methacrylic acid (86 g) was dissolved in 500 ml of dichloromethane, and 10 g of 4-dimethylaminopyridine was added thereto. Further, 102 g of 2-hydroxy- $\gamma$ -butyrolactone was gently added. The resulting solution was cooled on an ice bath, and 25 g of dicyclohexylcarbodiimide was further slowly added thereto. After stirring as such for 30 minutes, the ice bath was removed, and the temperature was spontaneously elevated to room temperature, followed by stirring at room temperature for 3 hours. After the reaction was completed, the precipitated powder was filtered, and the resulting filtrate was extracted with 10% aqueous hydrochloric acid. The extract was washed with an aqueous solution of sodium bicarbonate, and further with saturated saline. The resulting oil layer was concentrated, and purified by silica gel column chromatography to obtain 150 g of the desired monomer [II-A-2].

### SYNTHESIS EXAMPLE 2

#### Synthesis of Monomer [II-C-2]

Monomer [II-C-2] was synthesized in the same manner as with Synthesis Example 1 with the exception that Light Ester HO-MS manufactured by Kyoeisha Chemical Co., Ltd. was substituted for methacrylic acid in Synthesis Example 1.

### SYNTHESIS EXAMPLE 3

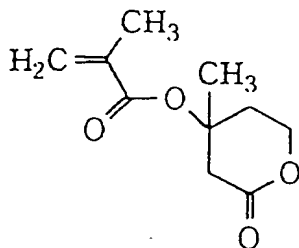
### Synthesis of Monomer [II-F-2]

Monomer [II-F-2] was synthesized in the same manner as with Synthesis Example 1 with the exception that a terminal carboxylic acid methacrylate synthesized by the reaction of 3-hydroxypropionic acid and Karenzu MOI manufactured by Showa Denko K. K. was used in place of methacrylic acid in Synthesis Example 1.

### SYNTHESIS EXAMPLE 4

#### Synthesis of Monomer 1 for Comparison

A monomer having the following structure was synthesized from mevalonolactone and methacrylyl chloride in accordance with the method described in Journal of Photopolymer Science and Technology, 9 (3), 509 (1996).



### SYNTHESIS EXAMPLE 5

#### Synthesis of Resin A

Tricyclodecanyl methacrylate (22.0 g), monomer [II-A-2] (13.6 g) and methacrylic acid (1.7 g) were dissolved in THF (87 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a

polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin A as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 36,000 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 6

##### Synthesis of Resin B

Tricyclodecanyl methacrylate (22.0 g), monomer [II-C-2] (25.1 g) and methacrylic acid (1.7 g) were dissolved in THF (114 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent

of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin B as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 37,500 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 7

##### Synthesis of Resin C

Tricyclodecanyl methacrylate (22.0 g), monomer [II-F-2] (32.9 g) and methacrylic acid (1.7 g) were dissolved in THF (133 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin C as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 39,000 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 8

##### Synthesis of Resin D

Tricyclodecanyl methacrylate (17.6 g), monomer [II-A-2] (10.2 g), t-butyl methacrylate (5.7 g) and methacrylic acid (1.7 g) were dissolved in THF (82 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin D as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 35,500 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 9

##### Synthesis of Resin E

Tricyclodecanyl methacrylate (17.6 g), monomer [II-C-2] (18.9 g), t-butyl methacrylate (5.7 g) and methacrylic acid (1.7 g) were dissolved in THF (102 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition



of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin E as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 37,200 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 10

##### Synthesis of Resin F

Tricyclodecanyl methacrylate (17.6 g), monomer [II-F-2] (19.8 g), t-butyl methacrylate (5.7 g) and methacrylic acid (1.7 g) were dissolved in THF (105 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin F as a white powder.

The GPC analysis of the resulting copolymer showed that

it had a weight-average molecular weight of 38,500 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 11

##### Synthesis of Resin G

Tricyclodecanyl methacrylate (22.0 g), monomer 1 for comparison (19.9 g) and methacrylic acid (1.7 g) were dissolved in THF (102 g), and then, the reaction solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes.

As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin G as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 35,600 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 12

##### Synthesis of Resin H

Tricyclodecanyl methacrylate (17.6 g), monomer 1 for comparison (12.0 g), t-butyl methacrylate (5.7 g) and methacrylic acid (1.7 g) were dissolved in THF (86 g), and then, the reaction

solution was heated to 65°C while passing a nitrogen gas therethrough for 30 minutes. As a polymerization initiator, 150 mg of V-65 manufactured by Wako Pure Chemical Industries, Ltd. was added thereto in 5 parts at intervals of 1 hour. After the final addition of the initiator, heating and stirring were continued as such for 4 hours. After the termination of heating, the temperature of the reaction solution was lowered to room temperature. The reaction solution diluted with 200 g of THF was reprecipitated with a mixed solvent of 4 liters of distilled water/2 liters of methanol, thus recovering the desired resin H as a white powder.

The GPC analysis of the resulting copolymer showed that it had a weight-average molecular weight of 34,500 in terms of standard polystyrene.

#### SYNTHESIS EXAMPLE 13

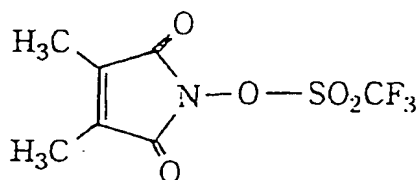
##### Synthesis of Photo Acid Generator (1)

Sodium hydroxide (8 g) and hydroxylamine hydrochloride (14 g) were dissolved in 200 ml of distilled water, and 25 g of dimethylmaleic anhydride added thereto. Then, the resulting solution was stirred at room temperature for 5 hours, followed by heat stirring at 100°C for 3 hours. After the reaction was completed, aqueous hydrochloric acid was added to the reaction solution. Then, the resulting solution was further saturated with sodium chloride, and thereafter extracted with ethyl acetate. The procedure of concentrating the extracted ethyl acetate

solution to one third, adding toluene to the concentrated solution and reconcentrating the solution to which toluene was added was repeated to isolate 15 g of N-hydroxymaleiminide.

In dichloromethane, 4.2 g of N-hydroxymaleiminide thus synthesized was dissolved, and 8.5 g of trifluoromethane-sulfonic acid anhydride was added dropwise on an ice bath for 1 hour. After 2.8 g of pyridine was further added dropwise for 2 hours, the ice bath was removed, and the temperature was elevated to room temperature, followed by stirring as such for 10 hours. After the reaction was completed, the reaction solution was washed with distilled water, and concentrated to conduct crystallization in hexane. The hexane layer was concentrated to obtain 10 g of the desired compound.

The following structure was confirmed by  $^{13}\text{C}$ NMR:



#### EXAMPLES AND COMPARATIVE EXAMPLES

In 2-heptanone, 1.2 g of each of resins A2 to H2 synthesized in Synthesis Examples described above and 0.25 g of photo acid generator (1) were dissolved so as to give a solid content of 14% by weight, and then, the resulting solution was filtered through a 0.1- $\mu\text{m}$  microfilter to prepare a positive type photoresist

composition solution. The formulation thereof is shown in Table 1 described below.

(Evaluation Tests)

The resulting positive type photoresist composition solution was applied onto a silicon wafer with a spin coater, and dried at 120°C for 90 seconds to prepare a positive type photoresist film having a thickness of about 0.5  $\mu\text{m}$ , which was exposed to an ArF excimer laser beam (193 nm). After exposure, heat treatment was carried out at 110°C for 90 seconds. Then, the photoresist film was developed with a 2.38% aqueous solution of tetramethylammonium hydroxide, and rinsed with distilled water to obtain a resist pattern profile.

[Relative Sensitivity]

Taking as a sensitivity an exposure which could reproduce a pattern having a width of 0.5  $\mu\text{m}$ , and taking the resist sensitivity of Example 1 as 1, the relative sensitivity of a resist other than that of Example 1 was determined by the following equation:

$$\frac{\text{Sensitivity other than that of Example 1}}{\text{Sensitivity of Example 1}}$$

[Pattern Profile]

The resist pattern profile obtained above was observed under a scanning electron microscope, and one showing a rectangular form was rated as  $\bigcirc$  and one showing a T-top form as  $\times$ .

[Adhesion]

Minimum Width of Remaining Thin Line: The resist pattern

profile obtained above was observed under a scanning electron microscope, and the adhesion was evaluated by the width of the thinnest remaining line. That is, higher adhesion results in remaining of a pattern having a thinner line width. Conversely, a pattern poor in adhesion can not adhere to a substrate as the linewidth becomes thinner, resulting in separation of the pattern.

Results thereof are shown in Table 1.

TABLE 1

	<u>Resin Used</u>	<u>Relative Sensiti- vity</u>	<u>Pattern Profile</u>	<u>Minimum Width of Remain- ing Thin Line</u>
Example 1	A	1.0	O	0.29
Example 2	B	0.9	O	0.30
Example 3	C	0.9	O	0.31
Example 4	D	0.6	O	0.28
Example 5	E	0.5	O	0.29
Example 6	F	0.6	O	0.30
Comparative Example 1	G	2.4	x	0.59
Comparative Example 2	H	1.7	x	0.60

Comparative Examples 4 and 5 each has problems in the relative sensitivity, the pattern profile and the adhesion. On the other hand, Examples 1 to 6 relating to the positive type photoresist compositions of the present invention are at levels satisfying all of them. That is, the positive type photoresist compositions of the present invention are suitable for lithography using far ultraviolet rays including ArF excimer laser exposure.

[Effect of the invention]

As described above, according to the present invention, there can be provided positive photoresist compositions which are sufficiently suitable, particularly, for light in the

wavelength region of 170 nm to 220 nm, high in sensitivity, excellent in adhesion and can give good resist pattern profiles.



[Name of document] ABSTRACT

[Summary]

[Problem] A positive type photoresist composition suitable for light in the wavelength region of 170 nm to 220 nm, high in sensitivity, excellent in adhesion to a substrate and can give good resist pattern profiles.

[Means to solve] A positive type photoresist composition comprising a resin having a specific ester group in its molecule and a compound generating an acid by irradiation of an active light ray or radiation.

[Chosen drawing] None